

REACTIVE
DYE
MIXTURES

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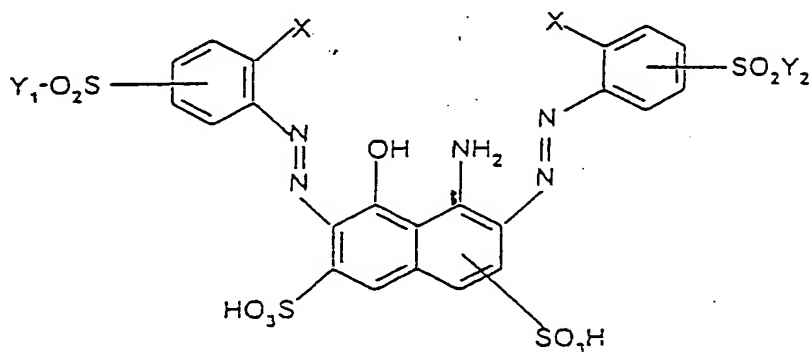
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REACTIVE DYE MIXTURES

This invention relates to mixtures of reactive dyes, in particular to mixtures of reactive dyes containing, as one component, a disazo dye derived from H-acid.

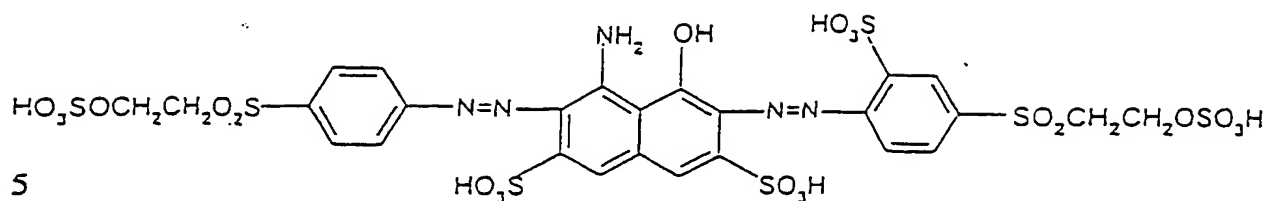
As is well known, reactive dyes contain at least one substituent capable of taking part in a reaction with a group present on a fabric to be dyed during the dyeing operation.

EP-A-0149170 discloses a range of dyes of the formula



in which one X is hydrogen and the other sulpho, each of Y_1 and Y_2 independently is a group $-\text{CH}=\text{CH}_2$, $-\text{CH}_2\text{CH}_2\text{OSO}_3\text{H}$, $-\text{CH}_2\text{CH}_2\text{SSO}_3\text{H}$, $-\text{CH}_2\text{CH}_2\text{Cl}$ or $-\text{CH}_2\text{CH}_2\text{OR}$, and R is a low molecular weight alkanoyl, benzoyl or benzenesulphonyl group, optionally substituted by a C_{1-4} alkyl, C_{1-4} alkoxy, halogen, carboxy or sulpho group.

A typical dye has the formula



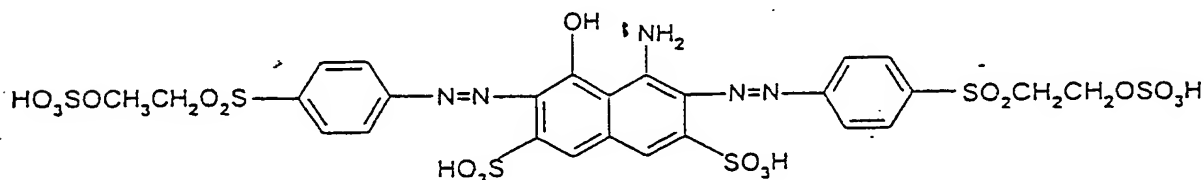
EP-A-0149170 refers only to individual dyes, not mixtures thereof.

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On the other hand, each of EP-A-0224224, EP-A-0679697, EP-A-0531968, EP-A-0668328 and EP-A-0600322 discloses

respective mixtures of dyes, one of which components is a disazo dye derived from H-acid. One particular example of

15 such a dye has the formula



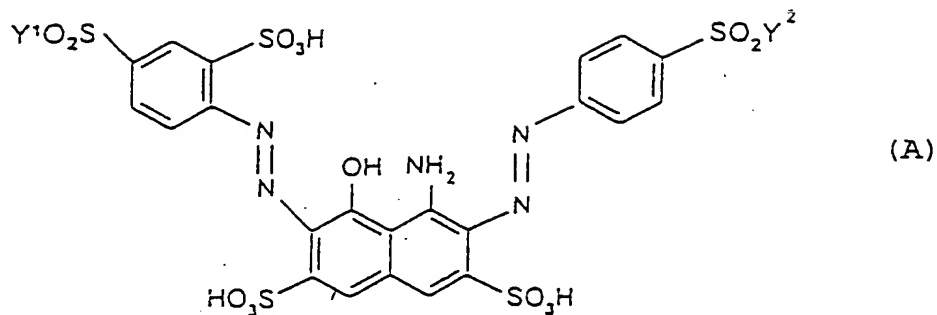
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This dye is available commercially as C.I.Reactive Black 5 and is added to other dyes as a dulling agent where appropriate.

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We find surprisingly that the fastness of a dye mixture can be improved if the dye mixture contains, as a component

thereof, a dye of the formula (A)



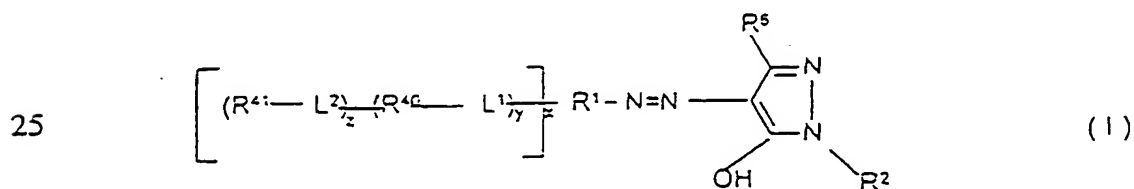
10 wherein each of Y^1 and Y^2 , independently, is a vinyl group or a group of the formula $-CH_2CH_2Q$ in which Q is a leaving group removable under alkaline conditions to provide a vinyl group.

15 The dye mixture may contain, in addition to component (A), any of a wide range of dyes.

More particularly, the present invention provides a dye mixture comprising a reactive dye of the formula (A), given and defined above; and

20 at least one reactive dye (B) selected from

(I) a monoazopyrazole dye of the formula



wherein R^1 is an aryl group selected from phenyl and naphthyl groups optionally having at least one substituent thereon, the substituents, or each substituent independently, being selected from a sulphonic acid group and a salt thereof, a C_{1-4} alkyl group, a C_{1-4} alkoxy group, a hydroxy group, a carboxyl group, a chlorine atom, a vinyl sulphonyl group and a group $SO_2CH_2CH_2Q^1$ in which Q^1 is a leaving group removable under alkaline conditions to provide a vinyl sulphonyl group;

10

R^2 is a phenyl or naphthyl group, optionally having at least one substituent thereon, the substituent, or each substituent, independently, being selected from a sulphonic acid group and a salt thereof, a C_{1-4} alkyl group, a C_{1-4} alkoxy group, a hydroxy group, a chlorine atom, a vinyl sulphonyl group, a group $SO_2CH_2CH_2Q^2$ in which Q^2 is a leaving group removable under alkaline conditions to provide a vinyl sulphonyl group, a group Het and a group L^5 -Het, where Het is an optionally substituted aromatic heterocyclic reactive or non-reactive group or a reactive or non-reactive group having an aliphatic chain and L^5 is as defined below; and

15

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R^6 is a methyl group, an amide group or a carboxyl group or a salt thereof;

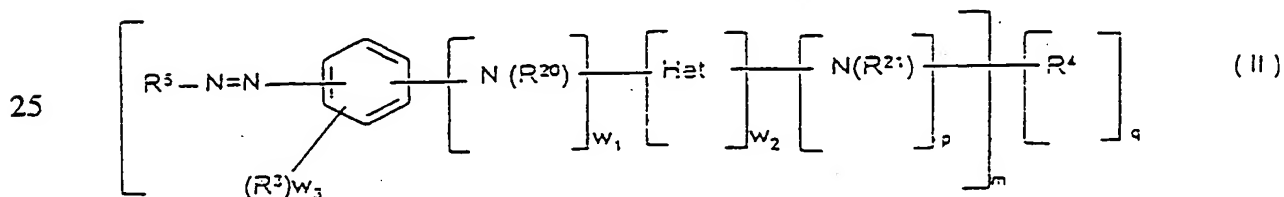
each of R^{40} and R^{41} , independently, is an aryl group selected from phenyl and naphthyl groups, each of which, independently, is optionally substituted by a vinylsulphonyl group, a group $SO_2CH_2CH_2Q^1$ in which Q^1 is a leaving group removable under alkaline conditions to provide a vinylsulphonyl group; or the group Het, where Het is as defined above;

at least one of R^1 , R^2 , R^{40} and R^{41} being, or having thereon at least one substituent which is, reactive;

each of L^1 , L^2 and L^5 independently is a linking group selected from $N(R^{20})$, in which R^{20} is hydrogen or C_{1-4} alkyl; $C(=O)$; $C(=O)-O$; $S(=O)_2$; $S(=O)-NH$; $C(=O)-NH$; and $NHC(=O)NH$; and

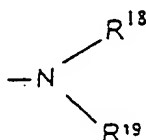
each of x , y and z , independently, is zero or 1; and, when the group R^1 is substituted by a hydroxy group ortho to the azo group, a metallized derivative thereof;

(II) a monoazo or disazo dye of the formula



wherein: Het is an optionally substituted aromatic heterocyclic reactive or non-reactive group or a reactive or non-reactive group having an aliphatic chain;

- 5 R^3 or each R^3 , independently, is a chlorine atom, a methyl group, a methoxy group, a sulphonic acid group or a salt thereof, or is an amino group of the formula



10

in which each of R^{18} and R^{19} , independently, is hydrogen, chloro, methyl, (C_{1-4} alkyl) carbonyl, aminocarbonyl, vinylsulphonyl or a group $SO_2CH_2CH_2Q^1$, in which Q^1 is as defined above;

15

- R^4 , or each R^4 independently, is hydrogen, a sulphonic acid group or a salt thereof, a C_{1-8} alkyl (preferably a C_{1-4} alkyl) group, a C_{1-4} alkoxy group, a vinyl sulphonyl group or a group $SO_2CH_2CH_2Q^2$ in which Q^2 is a
- 20 leaving group removable under alkaline conditions to provide a vinyl sulphonyl group, which C_{1-4} alkyl group or C_{1-4} alkyl moiety of the C_{1-4} alkoxy group is optionally interrupted by an oxygen atom to provide an ether group and is optionally substituted by a vinyl sulphonyl group or a
- 25 group $SO_2CH_2CH_2Q^2$, in which Q^2 is as defined above; or R^4 (or when q is 2, each R^4 independently) is a phenyl group optionally substituted by at least one sulphonic acid group

or a salt thereof or at least one group Het, where Het is as defined above; or R⁴ is a group Het, where Het is as defined above

5 R⁵ is an aryl group selected from phenyl and naphthyl groups each optionally substituted by at least one sulphonic acid group or, a salt thereof or at least one group Het, as defined above;

R²⁰ is a hydrogen atom or a C₁₋₄ alkyl group;

10 R²¹ is a hydrogen atom, a C₁₋₄ alkyl group, a sulphonic acid-C₁₋₄ alkyl group, a chloroalkylsulphonyl-C₁₋₄ alkyl group or a group Het, where Het is as defined above;

m is 1 or 2;

p is zero, 1 or 2;

15 q is zero, 1 or 2;

each of w₁ and w₂ is zero or 1; and

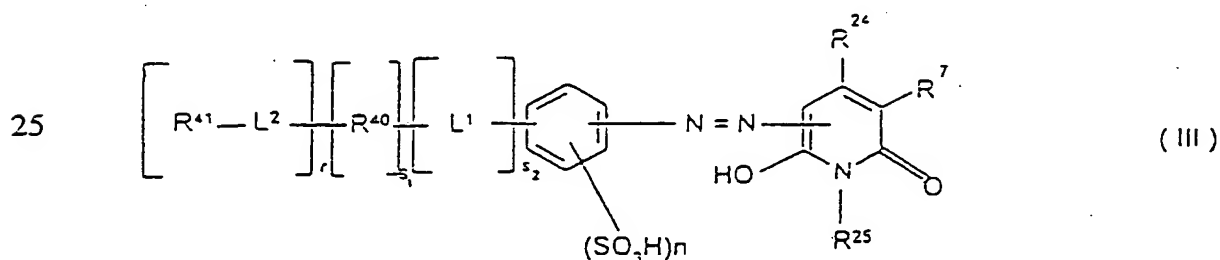
w₃ is 1, 2 or 3; and

when p is zero, q is zero;

at least one of R⁴, R⁵, R¹⁸, R¹⁹, R²¹ and Het being,

20 or having thereon at least one substituent which is, reactive;

(III) a monoazopyridone dye of the formula



wherein: each of R^{40} , R^{41} , L^1 and L^2 is as defined above;

R^7 is optionally present and is a cyano group or the group $-CH_2SO_3H$ or the group $-C(=O)NH_2$;

each of R^{24} and R^{25} , independently, is a hydrogen atom, a C_{1-4} alkyl group, a sulpho- C_{1-4} alkyl group, or a carboxyl group;

n is 1 or 2;

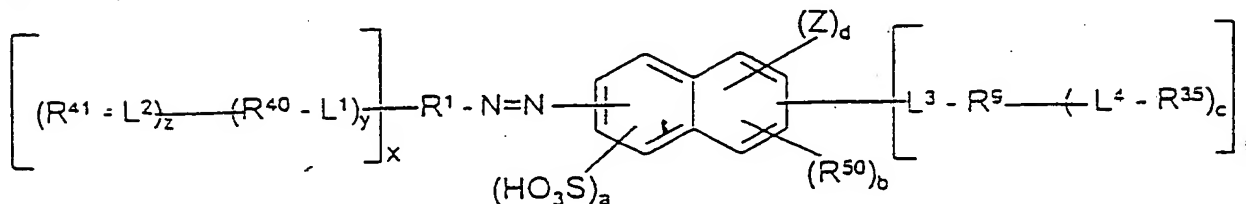
r is zero or 1; and

each of s_1 and s_2 is zero or 1; and when R^{40} is a phenyl or naphthyl group s_2 is 1;

at least one of R^{40} and R^{41} being, or having thereon at least one substituent which is, reactive;

(IV) a monoazonaphthyl dye of the formula

15



(IV)

20

wherein: each of R^1 , R^{40} , R^{41} , L^1 , L^2 , x , y and z is as defined above;

R^9 is $CH_3(C=O)-$, Het (as defined above) or an aryl group selected from phenyl and naphthyl, which Het or aryl group is optionally substituted by at least one substituent, the or each substituent, independently, being

selected from a sulphonic acid group and a salt thereof, a C₁₋₄ alkyl group, a C₁₋₄ alkoxy group, a hydroxy group, an amino group optionally substituted by at least one methyl or sulphato group, a vinyl sulphonyl group and a group

5 SO₂CH₂CH₂Q¹ in which Q¹ is as defined above;

R³⁵ is a C₁₋₄ alkyl or C₂₋₄ alkenyl group, which C₁₋₄ alkyl or C₂₋₄ alkenyl group is optionally substituted by at least one halogen atom, a sulphonic acid group or salt

10 thereof, a chloroalkylsulphonyl group, a vinylsulphonyl group or -SO₂CH₂CH₂Q¹, where Q¹ is as defined above and which C₁₋₄ alkyl or C₂₋₄ alkenyl group optionally additionally contains at least one oxygen or sulphur atom in the chain thereof; the group Het (as defined above); or an aryl group

15 selected from phenyl and naphthyl, which Het or aryl group is optionally substituted by at least one substituent, the substituent or each substituent independently, being selected from a sulphonic acid group and a salt thereof, a C₁₋₄ alkyl group, a C₁₋₄ alkoxy group, a halogen atom, a

20 hydroxy group, an amino group optionally substituted by at least one methyl or sulphato group, a vinylsulphonyl group, a vinylsulphonyloxyethyl group and a group SO₂CH₂CH₂Q¹ in which Q¹ is as defined above;

25 R⁵⁰ is a vinylsulphonyl group or a group SO₂CH₂CH₂Q¹ (in which Q¹ is as defined above);

at least one of R¹, R⁹, R³⁵, R⁴⁰, R⁴¹ and R⁵⁰ is, or

has thereon at least one substituent which is, reactive;

L^3 is a linking group selected from $N(R^{20})$, in which R^{20} is as defined above; CO; COO; NHCO; NHCONH; SO_2NH and SO_2 ;

L^4 is a linking group selected from $N(R^{21})$, in which R^{21} is as defined above, CO, COO, NHCO, NHCONH, SO_2NH and SO_2 ;

Z is hydroxy, amino or methylamino;

a is zero or 1-4;

b is zero or 1-3;

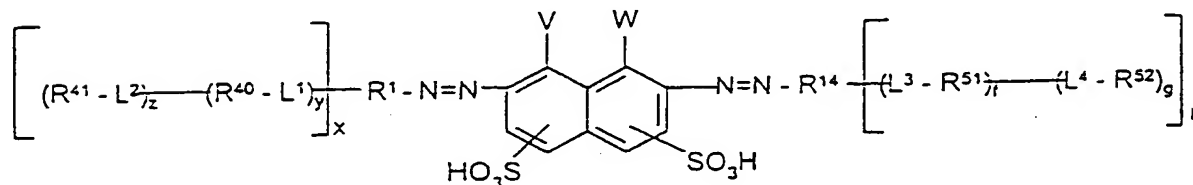
c is zero or 1;

d is zero, 1 or 2;

e is zero or 1; and

when each of R^1 and Z provides a hydroxyl group ortho to the azo group, a metallized derivative thereof;

(V) a disazoaminonaphthyl dye of the formula



(V)

wherein: each of R^1 , R^{40} , R^{41} , L^1 , L^2 , x, y and z is as defined above;

each of V and W, independently, is NH_2 or OH ;

5 R^{14} is an aryl group selected from phenyl and naphthyl groups optionally having at least one substituent thereon, the substituents, or each substituent independently, being selected from a sulphonic acid group and a salt thereof, a C_{1-4} alkyl group, a C_{1-4} alkoxy group, a hydroxy group, a vinyl sulphonyl group, a group $\text{SO}_2\text{CH}_2\text{CH}_2\text{Q}^1$ in which Q^1 is a leaving group removable under alkaline
10 conditions to provide a vinyl sulphonyl group;

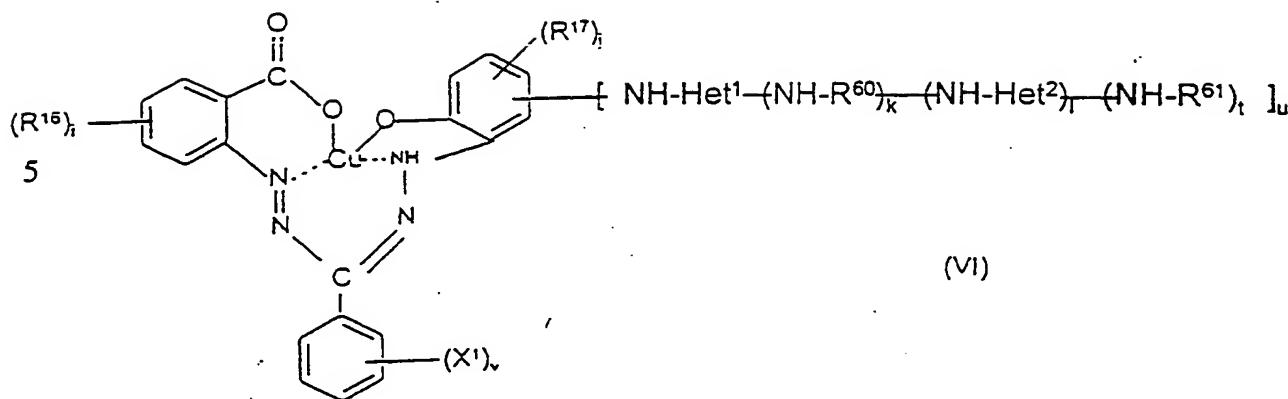
each of R^{51} and R^{52} independently is an aryl group selected from phenyl and naphthyl groups each of which is optionally substituted by a vinyl sulphonyl group, a group
15 $\text{SO}_2\text{CH}_2\text{CH}_2\text{Q}^1$ in which Q^1 is a leaving group removable under alkaline conditions to provide a vinyl sulphonyl group, or the group Het^3 , where Het^3 is an optionally substituted aromatic heterocyclic reactive group or a reactive group having an aliphatic chain;

20 each of L^3 and L^4 , independently, is a linking group selected from $\text{N}(\text{R}^{20})$, in which R^{20} is hydrogen or C_{1-4} alkyl; $\text{C}(=\text{O})$; $\text{C}(=\text{O})-\text{O}$; $\text{S}(=\text{O})_2$; $\text{S}(=\text{O})-\text{NH}$; $\text{C}(=\text{O})-\text{NH}$; and $\text{NHC}(=\text{O})\text{NH}$;

25 each of f, g and h, independently is zero or 1; and

at least one of R^{14} , R^{40} , R^{41} , R^{51} and R^{52} is, or has thereon at least one substituent which is, reactive;

(VI) a formazan dye of the formula.



10

wherein: each of R^{16} and R^{17} independently of one another, each R^{16} independently of one another and each R^{17} independently of one another, is a sulphonic acid group or a salt thereof, a vinyl sulphonyl group or a group $SO_2CH_2CH_2Q^1$ in which Q^1 is a leaving group removable under alkaline conditions to provide a vinyl sulphonyl group;

15

each of Het^1 and Het^2 , independently, is an optionally substituted aromatic heterocyclic reactive or non-reactive group or a reactive or non-reactive group having an aliphatic chain; and

20

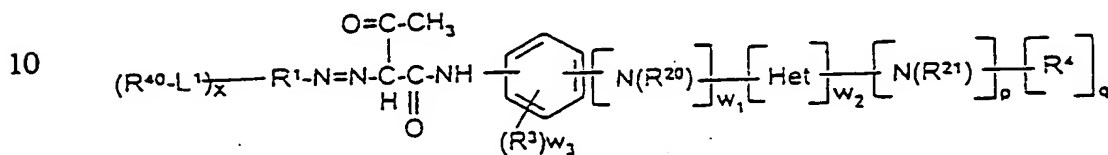
each of R^{60} and R^{61} , independently, is an aryl group selected from phenyl and naphthyl groups each of which is optionally substituted by a sulphonic acid group or a salt thereof, a vinylsulphonyl group or a group $SO_2CH_2CH_2Q^1$ in which Q^1 is as defined above;

25

X^1 is a sulphonic acid group or a salt thereof or halogen; each of i , j and v , independently, is zero, 1 or 2; and each of k , l , t and u , independently, is zero or 1; and

at least one of R^{16} , R^{17} , R^{50} , R^{51} , Het^1 and Het^2 is, or has thereon at least one substituent which is, reactive;

(VII) a dye of the formula

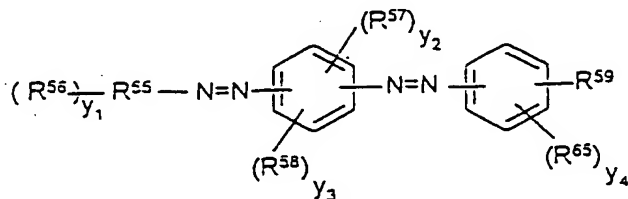


(VII)

wherein: each of R^1 , R^2 , R^3 , R^4 , R^{20} , R^{21} , R^{40} , L^1 , Het , x , p , q , w_1 , w_2 and w_3 is as defined above; and

at least one of R^1 , R^2 , R^3 , R^4 , R^{21} , R^{40} and Het is, or has thereon, at least one substituent which is, reactive;

(VIII) a disazo dye of the formula



(VIII)

wherein R⁵⁵ is an aryl group selected from phenyl and naphthyl groups;

R^{56} is a sulphonic acid group or a salt thereof or a reactive group selected from a vinyl sulphonyl group and a group $SO_2CH_2CH_2Q^1$ in which Q^1 is a leaving group removable under alkaline conditions to provide a vinyl sulphonyl group;

R^{57} is an amino group or a group NHR^A in which R^A is a C_{1-4} alkyl group;

10 R⁵⁸ is a sulphonic acid group or a salt thereof;

R⁵⁹ is a sulphonic acid group or a salt thereof, a reactive group selected from a vinyl sulphonyl group and a group SO₂CH₂CH₂Q² in which Q² is a leaving group removable under alkaline conditions to provide a vinyl sulphonyl group; or the group R⁵⁹ is a group Het or a group L¹⁰-Het, where Het is an optionally substituted aromatic heterocyclic reactive or non-reactive group;

R^{65} is a ureido group or a group $HNC(=O)R^B$ in which R^B is a C_{1-4} alkyl group;

20 L^{10} is a linking group selected from $N(R^{20})$, in which R^{20} is hydrogen or C_{1-4} alkyl; $C(=O)$; $C(=O)-O$; $S(=O)_2$; $S(=O)-NH$; $C(=O)-NH$; and $NHC(=O)NH$;

y_1 is zero, 1, 2 or 3;

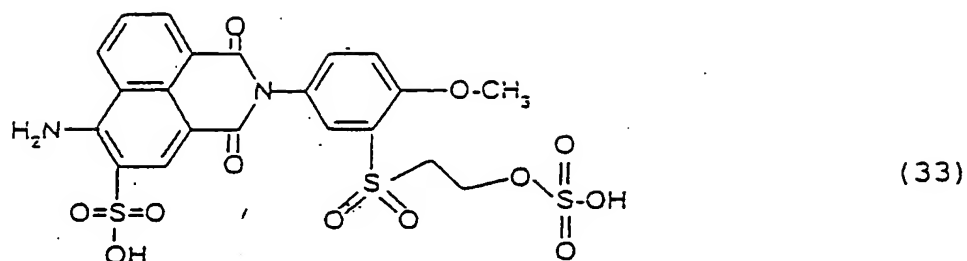
y_2 is zero, 1 or 2;

25 y_3 is zero or 1; and

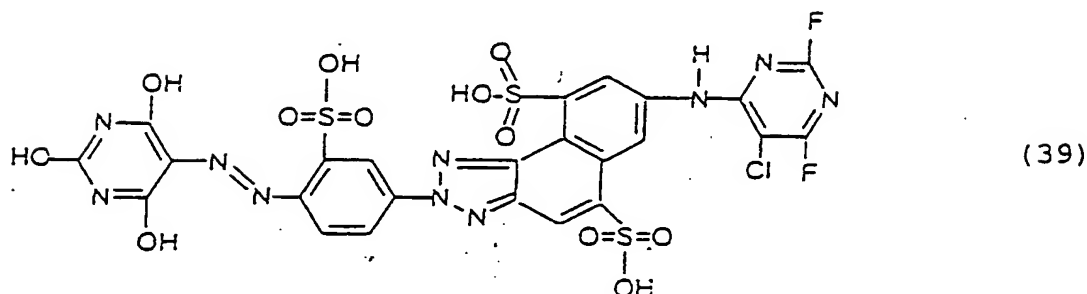
y_4 is zero or 1; and

at least one of R^{56} and R^{59} is a reactive group.

(IX) a dye of the formula



or



(X) a metal phthalocyanine dye of the formula



wherein: MPC is a metallophthalocyanine chromophore;

each of R^{70} and R^{71} , independently, is hydrogen or

C_{1-4} alkyl;

B is a hydrocarbon bridging group;

Het is a reactive heterocyclic group;

each of x_1 , x_2 and x_3 is a respective average value;

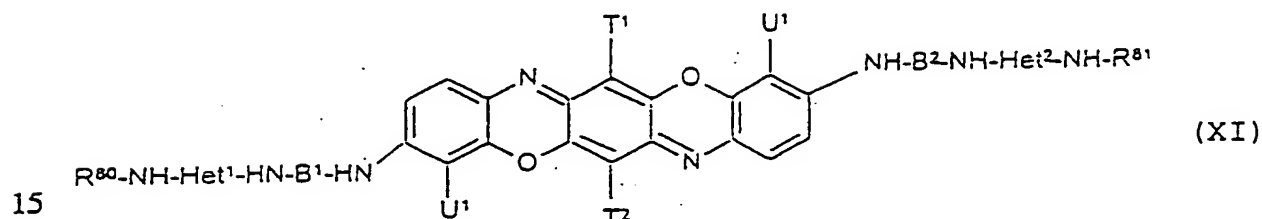
$$x_1 + x_2 + x_3 = 4;$$

5 x_1 is at least 1

x_2 is zero or 1; and

x_3 is at least 1; and

(XI) a triphenodioxazine dye of the formula (XI) (or a salt thereof)



wherein: each of B^1 and B^2 , independently, is a hydrocarbon bridging group;

20 U^1 is H or SO_3H ; and

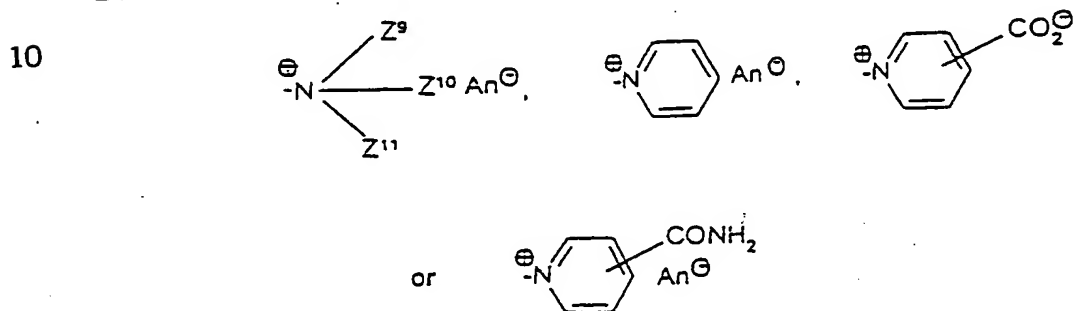
each of T^1 and T^2 , independently, is halo, C_{1-4} alkyl, or C_{1-4} alkoxy;

25 each of R^{80} and R^{81} is a phenyl group substituted by at least one sulphonic acid group or a salt thereof;

each of Het^1 and Het^2 is as defined above; and

at least one of Het¹ and Het² is a reactive group.

Referring to the dye of the formula (A), preferably at least one of Y¹ and Y² is the group -CH₂CH₂Q and Q is selected from chlorine, bromine, C₁₋₄-alkylsulfonyl, phenylsulfonyl, OSO₃H, SSO₃H, OP(O)(OH)₂, C₁₋₄-alkylsulfonyloxy, phenylsulfonyloxy, (C₁₋₄ alkyl) carbonyloxy, (C₁₋₄ dialkyl) amino or a radical of the formula



where Z⁹, Z¹⁰ and Z¹¹ are identical or different and are each, independently of one another, C₁₋₄ alkyl or benzyl and An[⊖] is in each case one equivalent of an anion. More preferably, each of Y¹ and Y² is the group HO₃SOCH₂CH₂.

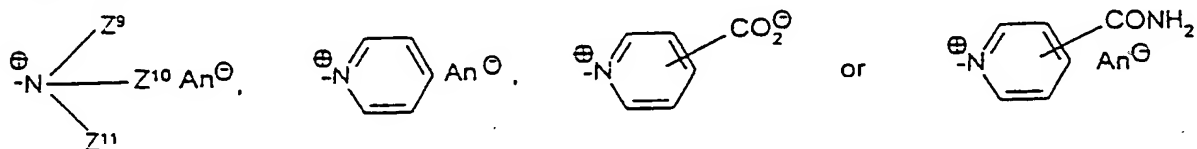
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Referring now to the reactive dye (B), dyes in one preferred range thereof contain a group Het, where Het is an optionally substituted aromatic heterocyclic reactive group derived from a halogen-substituted heterocyclic compound selected from 1,3,5-triazine, quinoxaline, phthalazine, pyrimidine, pyridazine and 2-(C₁₋₄ alkylsulphonyl) benzothiazole. More preferably, the aromatic heterocyclic reactive group is substituted and at

least one substituent is a halogen atom.

An alternative preferred range of reactive dyes (B) contains a group Het, where Het is a reactive group having an aliphatic chain and selected from acryloyl, mono-, di- or trichloroacryloyl, mono-, di- or tri- bromoacryloyl, -CO-CCl=CH-COOH, -CO-CH=CCl-COOH, 2-chloropropionyl, 1,2-dichloropropionyl, 1,2-dibromopropionyl, 3-phenylsulfonylpropionyl, 3-methylsulfonylpropionyl, 2-sulfatoethylaminosulfonyl, 2-chloro-2,3,3-trifluorocyclobutylcarbonyl, 2,2,3,3-tetrafluorocyclobutylcarbonyl, 2,2,3,3-tetrafluorocyclobutylsulfonyl, 2-(2,2,3,3-tetrafluorocyclobutyl)acryloyl, 1- or 2-alkyl- or 1- or 2-arylsulfonylacryloyl, or a radical of the formula SO₂-Y³, SO₂NH-Y³, CONH-L⁶-SO₂-Y³, or NHCONH-L⁶-SO₂-Y³ where L⁶ is C₁-C₄-alkylene or phenylene and Y³ is a vinyl group or a group of the formula CH₂CH₂Q³ in which Q³ is a leaving group removable under alkaline conditions to provide a vinyl group.

It is also preferred that, the reactive dye (B) has at least one of the groups Q¹ and Q² therein and the or each of groups Q¹ and Q² independently is selected from chlorine, bromine, C₁₋₄-alkylsulfonyl, phenylsulfonyl, OSO₃H, SSO₃H, OP(O)(OH)₂, C₁₋₄-alkylsulfonyloxy, phenylsulfonyloxy, (C₁₋₄ alkyl) carboxyloxy, (C₁₋₄ dialkyl) amino or a radical of the formula



where Z^9 , Z^{10} and Z^{11} are identical or different and are each, independently of one another, C_{1-4} -alkyl or benzyl and An^e is in each case one equivalent of an anion.

5

In a dye mixture wherein the reactive dye (B) is a monoazopyrazole dye of the formula (I), given and defined above, it is preferred that at least one of the group

10 $[(R^{41}-L^2)_z(R^{40}-L^1)_y]_xR^1$ and the group R^2 has at least one sulphonic acid group substituted thereon and at least the other of the group $[(R^{41}-L^2)_z(R^{40}-L^1)_y]_xR^1$ and the group R^2 has a group $-SO_2CH_2SO_2Q^2$ substituted thereon, Q^2 being as defined above.

15 In respective preferred ranges of the reactive dye (B) of the formula (I)

(i) x' is zero and the group R^1 is substituted by at least one of a sulphonic acid group and the group
20 $-SO_2CH_2SO_2Q^1$, wherein Q^1 is as defined above;

(ii) each of x , y and z is 1, each of L^1 and L^2 is NH, R^{40} is the group Het, where Het is a triazine ring substituted by a halogen atom and R^{41} is an optionally
25 substituted phenyl group.

(iii) each of x and z is 1, y is zero, L^2 is NH and R^{41} is the group Het, where Het is a difluorochloropyrimidinyl

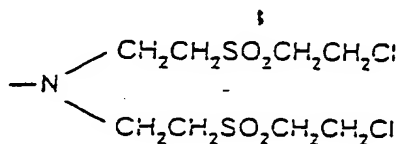
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group; and

- (iv) each of x and z is 1, y is zero, L² is CONH (in which the nitrogen atom is attached to the group R¹ and the carbon to the group R⁴¹) and R⁴¹ is the group Het, where Het is a 2,3-dichloroquinoxaline group.

In a reactive dye (B) of the formula (I), R² is preferably a phenyl or naphthyl group substituted by

- (i) at least one of a sulphonic acid group and the group -SO₂CH₂SO₂Q², where Q² is as defined in claim 1; or
- (ii) at least by the group NH-Het, where Het is a triazine ring substituted by a halogen atom and optionally substituted by the group



In a reactive dye (B) of the formula (I), the group R¹ may be substituted by a hydroxy group ortho to the azo group and the reactive dye (B) may then be in the form of a copper complex.

Reference is now made to a dye mixture wherein the reactive dye (B) is monoazo or disazo dye of the formula (II), given

and defined above.

In such a mixture it is preferred that in the reactive dye (B) of the formula (II), when m is 1 and R^4 is alkyl, R^4 is C_{1-4} alkyl.

It is also preferred that the group R^5 is an aryl group selected from phenyl and naphthyl groups each substituted by at least one sulphonic acid group or a salt thereof or by a group Het, wherein Het is a vinylsulphonyl group or a group $SO_2CH_2CH_2Q^1$ in which Q^1 is as defined above.

In an especially preferred reactive dye (B) of the formula (II), m is 1, so that the dye is a monoazo dye.

In preferred ranges of monoazo dyes (B) of the formula (II) in a mixture in accordance with the invention,

(i) each of w_1 , w_2 , p and q is zero, w_3 is at least 2, at least one of the groups R^3 is a sulphonic acid group and the group R^5 is an aryl group selected from phenyl and naphthyl groups each substituted by a vinylsulphonyl group or a group $-SO_2CH_2CH_2Q^1$, where Q^1 is as defined above.

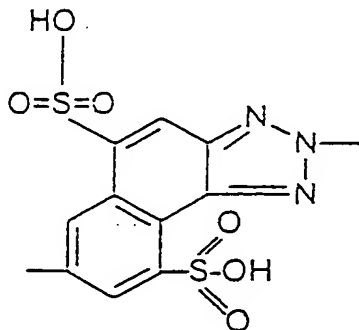
(ii) each of w_1 and w_2 is zero, each of p and q is 1, R^{21} is hydrogen and R^4 is selected from a triazine ring substituted by at least one halogen atom and optionally additionally substituted by an amino group; and a pyrimidine group substituted by at least one halogen atom and optionally additionally substituted by a methyl group;

(iii) each of w_1 , w_2 , p and q is 1, R^{20} is hydrogen, Het

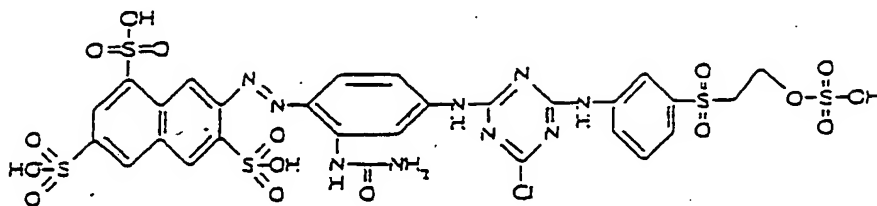
is a triazine ring substituted by a halogen atom, R^{21} is hydrogen and R^4 is selected from a phenyl group or a group $-SO_2CH_2CH_2Q^1$, where Q^1 is as defined above, and a straight or branched C_{2-4} alkylene chain substituted by a substituent
 5 selected from a hydroxyl group; a sulphonic acid group or salt thereof; a vinylsulphonyl group, a group $-SO_2CH_2CH_2Q^2$, where Q^2 is as defined above; and a pyrimidinylamino group in which the pyrimidinyl group is substituted by at least one halogen atom and optionally additionally by a methyl
 10 group; and which straight or branched C_{2-4} alkylene group optionally contains a hetero atom selected from O, S and N(H);

(iv) each of w_1 and w_2 is zero, each of p and q is 1
 15 and each of R^{21} and R^4 is the group OSO_3H ; and

(v) w_1 is zero, w_2 is 1, p is 1, q is 1, R^{21} is hydrogen, R^4 is a pyrimidinyl group substituted by at least one halogen atom and optionally additionally substituted by
 20 a methyl group and Het is a non-reactive heterocyclic group of the formula



An especially preferred dye mixture contains a dye of the formula (44) as the reactive dye (B) of formula (II)



Reference is now made to a dye mixture wherein the reactive dye (B) is a monoazopyridone dye of the formula (III), given and defined above.

In respective preferred ranges of the reactive dye (B) of the formula (III),

(i) each of r , s_1 and s_2 is 1, each of L^1 and L^2 is NH, R^{40} is a triazine ring substituted by a halogen atom and R^{41} is selected from a phenyl group substituted by at least one of a chlorine atom, a sulphonic acid group or a salt thereof, a vinylsulphonyl group or a group $-SO_2CH_2CH_2Q^1$, where Q^1 is as defined above; and a straight or branched chain C_{2-4} alkylene group optionally containing at least one oxygen atom and substituted by a vinylsulphonyl group or a group $-SO_2CH_2CH_2Q^1$, where Q^1 is as defined above;

(ii) each of r and s_1 is 1, s_2 is zero, L^2 is NH, R^{41} is

a pyrimidinyl group substituted by at least one halogen atom and optionally additionally substituted by a methyl group and R^{40} is a naphtho-(1,2-d)-1,2,3-triazole substituted by at least one sulphonic acid group or salt thereof; and

(iii) each of r_1 , s_1 and s_2 is 1, L^1 is CONH (in which the carbon atom is attached to the group R^{40}), L^2 is NH, R^{40} is an optionally substituted phenyl group and R^{41} is a pyrimidinyl group substituted by at least one halogen atom and optionally additionally substituted by a methyl group.

Reference is now made to a dye mixture wherein the reactive dye (B) is a monoazonaphthyl dye of the formula (IV), given and defined above.

In one preferred range of such dyes,

(i) x is zero, d is 1 and a or b is 1. More preferably e is zero.

In other preferred respective ranges,

(ii) x is 1, y is zero, z is 1, L^2 is NH and R^{41} is a pyrimidinyl group substituted by at least one halogen atom and optionally additionally substituted by a methyl group;

(iii) x is 1, y is zero, z is 1, L^2 is CONH (with the

carbon atom attached to the group R^1 and the nitrogen atom to the group R^{41}) and R^{41} is a phenyl group substituted by a vinylsulphonyl group or a group $-SO_2CH_2CH_2Q^1$, where Q^1 is as defined above; and

5

(iv) each of x , y and z is 1, each of L^1 and L^2 is NH, R^{40} is a triazine ring substituted by a halogen atom and R^{41} is an aromatic group selected from phenyl and naphthyl groups each substituted by at least one of a sulphonic acid group or a salt thereof, a vinylsulphonyl group and the group $-SO_2CH_2CH_2Q^1$, where Q^1 is as defined above.

10

In such ranges (ii) - (iv) of dyes (B) of the formula (IV), more preferably, e is zero.

15

In other preferred ranges of the reactive dye (B) of the formula (IV),

(v) e is 1, c is zero, L^3 is CONH (where either the nitrogen or carbon atom thereof is attached to the group R^9) and R^9 is a methyl group;

20

(vi) e is 1, c is zero, L^3 is CONH (where either the nitrogen or carbon atom thereof is attached to the group R^9) and R^9 is a phenyl group optionally substituted by at least one substituent, the or each substituent being selected from methoxy, carboxyethyl, sulphoethyl, carboxyethenyl, 1,2-dibromoalkyl, chloroethylsulphonyl, vinylsulphonyl, a

25

group of the formula $-\text{SO}_2\text{CH}_2\text{CH}_2\text{Q}^1$, where Q^1 is as defined above and a 2,3-dichloroquinoxaline group.

(vii) e is 1, c is 1, L^3 is CONH (where either the nitrogen or carbon atom thereof is attached to the group R^9), R^9 is a phenyl group substituted at least by the group $\text{L}^4\text{-R}^{35}$, where L^4 is NH and R^{35} is a vinyl group optionally substituted by a halogen atom or a pyrimidinyl group substituted by a halogen atom and optionally additionally substituted by a methyl group; and

(viii) e is 1, c is zero, L^3 is $\text{N}(\text{R}^{20})$, where R^{20} is as defined above (and is more preferably a hydrogen atom or a methyl group) and R^9 is a vinylsulphonyl group, a group $-\text{SO}_2\text{CH}_2\text{CH}_2\text{Q}^1$ wherein Q^1 is as defined in claim 1, or a pyrimidinyl group substituted by a halogen atom and optionally additionally substituted by a methyl group.
In yet another preferred range

(ix) e is 1, c is zero, L^3 is $\text{N}(\text{R}^{20})$, where R^{20} is as defined above and R^9 is a triazine ring substituted by at least one halogen atom. In this range the triazine ring is preferably substituted by two halogen atoms or by one halogen atom and a morpholinyl group.

In another preferred range,

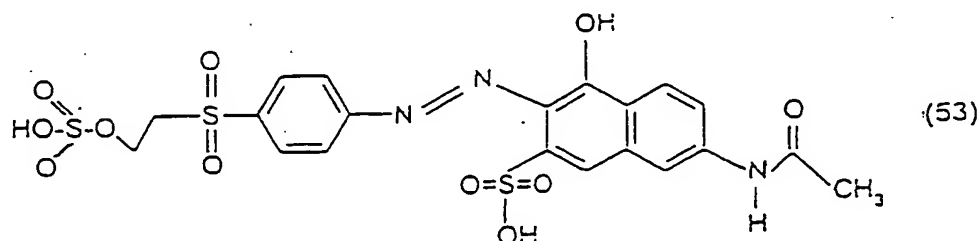
(x) e is 1, c is 1, L^3 is $\text{N}(\text{R}^{20})$, where R^{20} is as

defined above, L^4 is the group R^{21} , where R^{21} is as defined above, and R^{35} is selected from a phenyl group optionally substituted by a sulphonic acid group or salt thereof, a halogen atom, a vinylsulphonyloxyalkyl group, a vinylsulphonyl group or the group $-SO_2CH_2CH_2Q^1$, where Q^1 is as defined above; and a C_{1-4} alkyl group optionally substituted by a vinylsulphonyl group, the group $-SO_2CH_2CH_2Q^1$, where Q^1 is as defined above, a sulphonic acid group or a salt thereof or a chloroalkylsulphonyl group, which C_{1-4} alkyl group optionally additionally contains at least one oxygen or sulphur atom in the chain thereof.

In dye mixtures containing a reactive dye (B) of the formula (IV) within the above ranges x is preferably zero.

In the reactive dye (B) of the formula (IV), each of the groups R^1 and the naphthalene nucleus may be substituted by a respective hydroxyl group ortho to the azo group and the reactive dye (B) may then be in the form of a copper complex thereof.

An especially preferred dye mixture contains a dye of the formula (53) as the reactive dye (B)



Reference is now made to a dye mixture wherein the reactive dye (B) is a disazo dye of the formula (V), given and defined above. In such dyes, the respective sulphonic acid groups on the naphthalene nucleus are preferably in the 3- and 6- positions (i.e. such dyes are preferably derived from H-acid).

In one preferred range of dyes of the formula

10

(i) V is amino, W is hydroxy, each of R^1 and $R^{1'}$ is a phenyl group substituted by at least one substituent, the or each substituent independently being selected from a sulphonic acid group or a salt thereof, a vinyl sulphonyl group and a group $SO_2CH_2CH_2Q^1$, where Q^1 is as defined above and $R^{1'}$ is optionally additionally substituted by at least one methoxy group.

15

It is also preferred, especially for one sub-range within the range (i), that each of x and h is zero. Such a range of dyes includes those of the formula (A) and a mixture in accordance with the invention may indeed contain only dyes of the formula (A), one such dye of the mixture being regarded as a dye of the formula (A) and at least one other such dye of the mixture being regarded as a dye of the formula (V).

25

In an alternative preferred range of dyes of the formula

(V), especially for another sub-range within the range (i), at least one of x and h is 1 and more preferably each of x and h is 1.

- 5 In a preferred sub-range (ii) of dyes (B) of the formula (V), within the range (i), x, y and z is 1, each of L^1 and L^2 is NH, R^{40} is a triazine ring substituted by a halogen atom and R^{41} is a phenyl group substituted by at least one substituent, the or each substituent independently being
10 selected from a sulphonic acid group or a salt thereof, a vinylsulphonyl group and a group $SO_2CH_2CH_2Q^1$, where Q^1 is as defined above.

- In the preferred ranges (i) and (ii) above, more
15 preferably, each of f, g and h is 1, each of L^3 and L^4 is NH, R^{51} is a triazine ring substituted by a halogen atom and R^{52} is a phenyl group substituted by at least one substituent, the or each substituent independently being
selected from a halogen atom, a sulphonic acid group or a
20 salt thereof, a vinylsulphonyl group and a group $SO_2CH_2CH_2Q^1$, where Q^1 is as defined above.

- In a preferred range (iii) of reactive dyes (B) of the formula (V), V is amino, W is hydroxy, h is zero and R^{14} is
25 a naphthalene group substituted by at least one sulphonic acid group. More preferably, in this range (iii), each of x, y and z is 1, R^1 is a phenyl group optionally substituted by a sulphonic acid group or a salt thereof, each of L^1 and

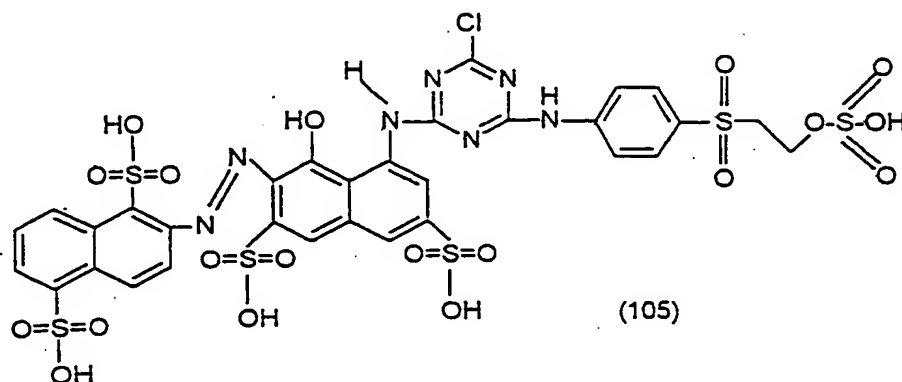
L^2 is NH, R^{40} is a triazine ring substituted by a halogen atom and R^{41} is a phenyl group substituted by at least one substituent, the or each substituent independently being selected from a sulphonic acid group or a salt thereof, a vinylsulphonyl group and a group $SO_2CH_2CH_2Q^1$, where Q^1 is as defined above.

In a preferred range (iv) of the reactive dyes (B) of the formula (V), V is amino, W is hydroxy, h is 1, f is zero, g is 1, L^4 is NH and R^{52} is the group Het³, where Het³ is a substituted aromatic heterocyclic group. In this range (iv), more preferably the group Het³ is a pyrimidinyl group substituted by at least one halogen atom and optionally additionally substituted by a methyl group and still more preferably x is zero and R^1 is a phenyl group substituted by a vinylsulphonyl group or $SO_2CH_2CH_2Q^1$, where Q^1 is as defined above.

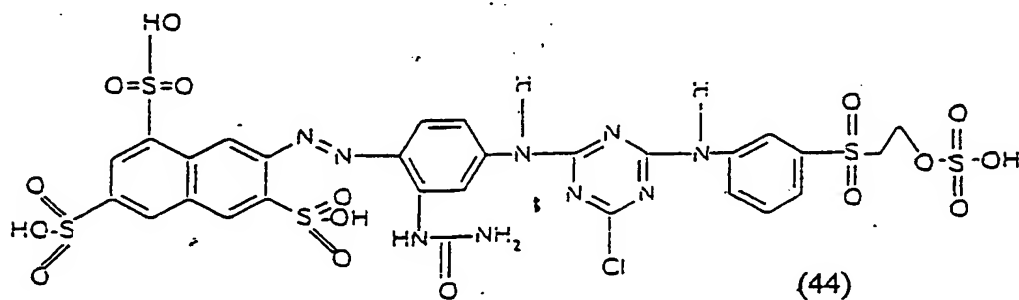
In a preferred range (v) of the reactive dyes (B) of the formula (V), V is amino, W is hydroxy, h is 1, f is zero, g is 1, L^4 is NHCO (where either the nitrogen or carbon atom thereof is attached to the group R^{14}) and R^{52} is the group Het³, where Het³ is a reactive group having an aliphatic chain. More preferably, in this range (v), the group Het³ is a vinylsulphonyl group or $SO_2CH_2CH_2Q^1$, where Q^1 is as defined above and still more preferably x is zero and R^1 is a phenyl group substituted by a vinylsulphonyl group or

$\text{SO}_2\text{CH}_2\text{CH}_2\text{Q}^1$, where Q^1 is as defined above.

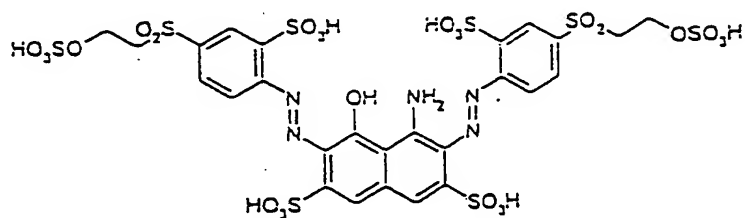
One especially preferred dye mixture contains a dye of the formula (105) as a dye of the formula (V)

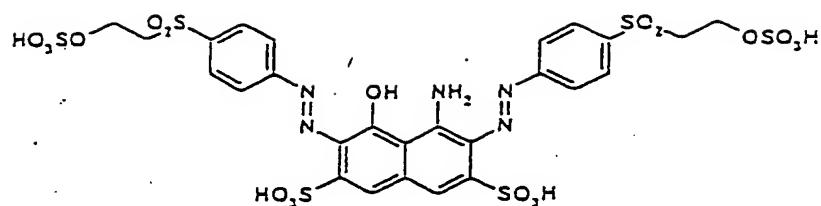


and more preferably additionally contains a dye of the formula (44) as another dye (B), of the formula (II)



20 Another especially preferred dye mixture contains at least one and more preferably both of the dyes of the formulae (163) and (167)





(167)

Reference is now made to a dye mixture wherein the reactive dye (B) is a formazan dye of the formula (VI), given and defined above.

In preferred respective ranges of the reactive dye (B) of the formula (VI)

(i) each of u and v is zero, i is 1, R^{16} is a sulphonic acid group or a salt thereof, j is 2 and one R^{17} is a sulphonic acid group or a salt thereof and the other R^{17} is a vinylsulphonyl group or $SO_2CH_2CH_2Q^1$, where Q^1 is as defined above; and

(ii) v is zero, i is 1, R^{16} is a sulphonic acid group or a salt thereof, j is 1, R^{17} is a sulphonic acid group, u is 1 and Het¹ is a triazine ring substituted by a halogen

atom. In one preferred sub-range within the range (ii), each of k and l is zero, t is 1 and R^{61} is a phenyl group substituted by at least one sulphonic acid group or a salt thereof, while in another preferred sub-range with the range (ii), each of k , l and t is 1, each of R^{60} and R^{61} independently is a phenyl group substituted by at least one sulphonic acid group or a salt thereof and Het^2 is a triazine ring substituted by a halogen atom. In yet another preferred sub-range within the range (ii), each of k and t is zero, l is 1 and Het^2 is a reactive group having an aliphatic chain.

Reference is now made to a dye mixture wherein the reactive dye (B) is a dye of the formula (VII), given and defined above.

In one preferred range of such dyes, x is zero and each of p , q , w and w_2 is 1. More preferably, in such a range, R^1 is a naphthalene ring substituted by at least one sulphonic acid group. It is also preferred that, in such a range, w_3 is 1 and R^3 is a methoxy group. Moreover, a preferred group of R^{20} is hydrogen and preferred groups of R^{21} are hydrogen, methyl and ethyl. A preferred group R^4 is a phenyl group substituted by at least one sulphonic acid group.

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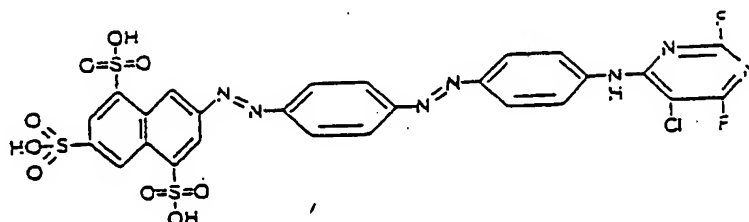
In another preferred range of such dyes (VII), each of p , q , w_1 and w_2 is zero. More preferably, in such a range, w_3

- is 3 and at least one of R^3 is a sulphonic acid group.
- Other groups of R^3 are preferably methyl, methoxy, amino or further sulphonic acid groups. It is also preferred that where, in such dyes, x is 1, R^1 is a phenyl or naphthyl
- 5 group substituted by at least one sulphonic acid group, L^1 is NH and R^{40} is a reactive halopyrimidine group, especially a group containing at least one, more especially at least two fluorine atoms and particularly a
- 10 difluorochloropyrimidine group, and that where, in such dyes x is zero, R^1 is a phenyl group substituted by a vinyl sulphonyl group or $SO_2CH_2CH_2Q^1$, where Q^1 is as defined above and optionally additionally substituted by at least one methoxy group.
- 15 Reference is now made to a dye mixture wherein the reactive dye (B) is a disazo dye of the formula (VIII), given and defined above.

In one preferred range of such dyes,

- 20 R^{55} is a naphthyl group;
- R^{56} is a sulphonic acid group or a salt thereof;
- R^{59} is a group L^{10} -Het, where L^{10} is the group N(H)- and Het is a reactive heterocyclic group substituted by at least one halogen atom;
- 25 y_1 is 1, 2 or 3; and
- each of y_2 , y_3 and y_4 is zero.

A particularly preferred such disazo dye of the formula (VIII) in a dye mixture embodying the invention has the formula



(71)

10

In another preferred range of such dyes of the formula (VIII)

R^{55} is a phenyl group;

the group R^{56} or each group R^{56} independently is a
 15 sulphonic acid group or a salt thereof or is a reactive group selected from a vinyl sulphonyl group and a group $SO_2CH_2CH_2Q^2$ in which Q^2 is as defined above;

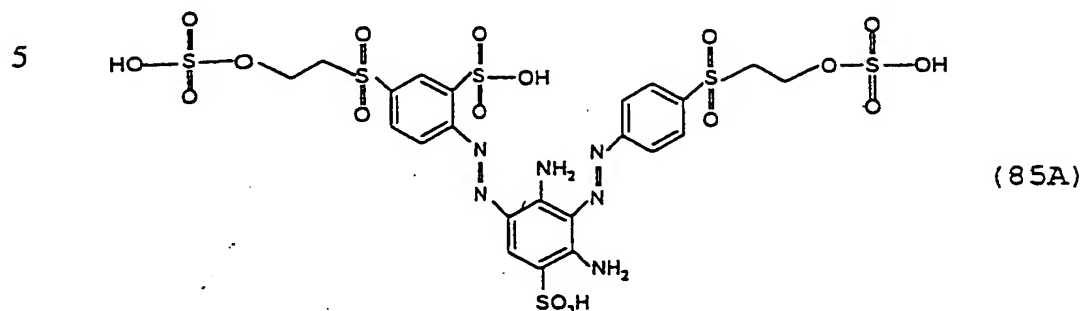
y_1 is 1 or 2; and

at least one group R^{56} is a said reactive group or the
 20 group R^{59} is or includes a reactive group.

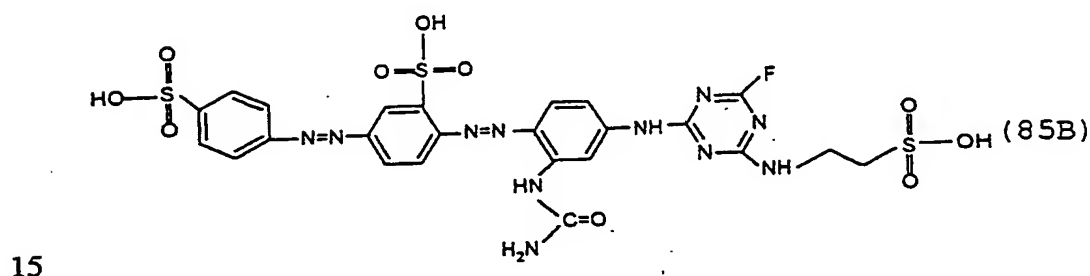
More preferably, at least one group R^{56} or the group R^{59} is a reactive group selected from a vinyl sulphonyl group and a group $SO_2CH_2CH_2Q^2$ in which Q^2 is as defined above; or
 25 at least one group R^{56} is a sulphonic acid group or a salt thereof and R^{59} is the group L^{10} -Het, where L^{10} is the group N(H)- and Het is a reactive triazine group substituted by a

halogen atom and additionally by the group $\text{NHCH}_2\text{CH}_2\text{SO}_3\text{H}$.

Especially preferred dyes have the formulae



10 and



Reference is now made to a dye mixture wherein the reactive dye (B) is a phthalocyanine dye of the formula (X), given and defined above.

20

Preferably, in the reactive dye (B) of the formula (X), respective average values of x_1 , x_2 and x_3 are x_1 is 3, x_2 is zero and x_3 is 1, three of the four isoindole rings of the phthalocyanine have a respective sulphonic acid substituent (or a salt thereof) thereon and the other isoindole ring has a group $\text{SO}_2\text{NH-B-NH-Het}$ substituted thereon. More preferably B is a straight or branched C_{2-4} alkylene group

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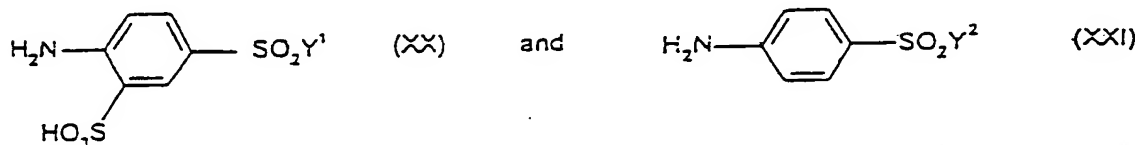
and Het is a triazine ring substituted by at least one halogen atom and optionally additionally substituted by a methoxy group.

- 5 Reference is now made to a dye mixture wherein the reactive dye (B) is a triphendioxazine dye of the formula (XI), given and defined above, or a salt thereof.

- 10 Preferably, in such a reactive dye (B) of the formula (XI), each of T^1 and T^2 is a halogen atom, each U^1 is a sulphonic acid group or a salt thereof, each of B^1 and B^2 independently is a straight or branched C_{2-4} alkylene group, each of Het^1 and Het^2 independently is a triazine ring substituted by a halogen atom and each of R^{80} and R^{81}
- 15 independently is a phenyl group substituted by at least one sulphonic acid group or a salt thereof.

The dyes of the formula (A) can be prepared by diazotising each of the amines (XX) and (XXI)

20



- wherein each of Y^1 and Y^2 is as defined above and firstly
- 25 coupling the diazotised amine (XXI) under strongly acid conditions (pH 1-2) to H-acid to provide an azo group ortho to the amine group and thereafter coupling the diazotised

amine (XX) under slightly acidic, neutral or alkaline conditions (pH 6-7) to the H-acid to provide an azo group ortho to the hydroxy group.

- 5 The diazotisation reactions may each be carried out by adjusting the pH of the amine with a buffer to about 5.3 - 6, adding an aqueous solution of hydrochloric acid and ice to cool to 0-5°C and then adding a sodium nitrite solution.
- 10 The coupling reactions may each be carried out by adjusting the pH as described above and allowing reaction to take place at a temperature of from 4 to 8°C for at least 3 hours.
- 15 These and other methods of preparing the dyes of the formula (A) are described in EP-A-0149170.

Likewise disazo dyes (B) of the formula (V) may be prepared in an analogous manner. Methods of preparation of such dyes are also disclosed in DE-A-3875658 and DE-A-3622080.

Dyes (B) of the formula (I) may be prepared by the methods disclosed in DE-A-3717667.

- 25 Dyes (B) of the formula (II) may be prepared by the method disclosed in DE-A-3927790, DE-A-3515651 and EP-A-0761768.

Dyes (B) of the formula (III) may be prepared by the methods disclosed in US-A-4618671, DE-A-3717814 and DE-A-

3829595.

Dyes (B) of the formula (IV) may be prepared by the method disclosed in US-A-4841031, EP-A-0343262 and EP-B-0776947.

5

Dyes (B) of the formula (VI) may be prepared by the methods disclosed in DE-A-3737536, DE-A-3743236 and DE-A-3840653.

10

Dyes (B) of the formula (X) may be prepared by the methods disclosed in WO-A-98/49240.

Dyes (B) of the formula (XI) may be prepared by the methods disclosed in DE-A-3423581 and EP-A-0773264.

15

Examples of dyes (B) of the formula (VII) are CI Reactive Yellow 57, CI Reactive Yellow 106, CI Reactive Yellow 160 and CI Reactive Yellow 167, all commercially available.

20

A preferred dye mixture in accordance with the invention comprises, by weight of the total weight of the dyes, from 10 - 99.5% by weight, inclusive of component (A), given and defined above, and from 0.5 to 90% by weight inclusive of component (B), given and defined above. Respective progressively more preferred ranges are as follows:

25

10 - 99% by weight, inclusive of component (A) and from 1 to 90% by weight, inclusive of component (B);

from 10 - 98.5% by weight, inclusive, of component (A) and
from 1.5 - 90% by weight, inclusive, of component (B);

from 10 - 97% by weight, inclusive, of component (A) and
5 from 3 - 90% by weight, inclusive, of component (B);

from 10 - 95% by weight, inclusive, of component (A) and
from 5 - 90% by weight, inclusive, of component (B);

10 from 10 - 90% by weight, inclusive, of component (A) and
from 10 - 90% by weight, inclusive, of component (B);

from 15 - 90% by weight, inclusive, of component (A) and
from 10 - 85% by weight, inclusive, of component (B);

15 from 20 - 90% by weight, inclusive, of component (A) and
from 10 - 80% by weight, inclusive, of component (B);

from 30 - 90% by weight, inclusive, of component (A) and
20 from 10 - 70% by weight, inclusive, of component (B); and

In an especially preferred mixture, component (B) is a mixture of dyes (B).

25 Mixtures embodying the invention can be prepared by merely mixing the individual dyes or, in some cases, by synthesis using a mixture of diazotising components. This method is especially suitable when component (B) is at least one dye of the formula (V). The dye mixture may be isolated, for

example, by spray drying or salting out.

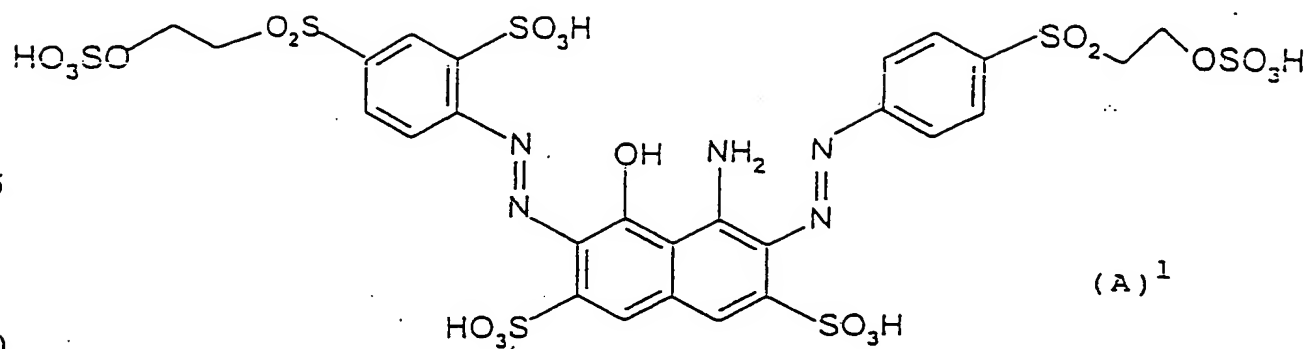
The mixtures can be used to dye or print on substrates containing a hydroxyl group or nitrogen atom, for example,
5 silk, leather, wool, polyamides, polyurethanes and cellulosic materials, especially cotton.

The mixtures provide excellent properties including resistance to modern peroxide based detergents, fastness to
10 repeat washing, good light fastness, excellent wash-off, good build-up, good compatibility of the dyes with one another and a robustness to process variables.

The reactive dye (A) alone gives a navy shade on cotton and
15 may be mixed with at least one yellow, orange, red or blue reactive dye (B) to give a forest green, navy, brown or black shade.

The mixtures have outstanding properties in comparison with
20 known mixtures, for example CI Reactive Black 5, referred to above, which is often used in a mixture with other dyes as a dulling agent.

Preferred embodiments of the invention will now be
25 described in more detail with reference to the following Examples, in which the numbers assigned to the dyes are those given in Table 2 and all parts are by weight unless otherwise stated. In the Examples, dye A has the formula

Example 1:

75 parts of dye (A)¹, 20 parts of dye (167) and 5 parts of dye (163) were mixed. The mixture was used to dye cotton, by application of cold pad batch and warm exhaust (40, 50 or 60°C) techniques as described below, in a navy shade resulting in good light fastness and fastness to repeated washing.

Exhaust application:

100g of cotton fabric were dyed in a dyebath that contained 1000 ml water, 12g of the mixture of Example 1, 2.5g sodium carbonate, 1g 32 weight% sodium hydroxide solution and 60g sodium sulphate decahydrate. The dyeing was started at 30°C, the temperature was raised to 50°C over a period of 30 minutes and the dyeing was continued for a further 60 minutes at this temperature. After cooling to room temperature the dyeing was rinsed and boiled with detergent, and dried.

Cold pad-batch application:

At room temperature woven cotton fabric was soaked in a padder with dye liquor that contained per 1000g dye liquor 60g of dye mixture of Example 1, 50g sodium silicate (38° B'e) and 30g 32 weight% sodium hydroxide solution.

- 5 After 70% pick-up the paddings are rolled and covered with cling film. After storing for 8h at room temperature the paddings are removed from the cling film, rinsed in cold water, hot rinsed with detergent, and dried.

10 Example 2:

- 60 parts of dye (A)¹, 24 parts of dye (44) and 16 parts of dye (105) were mixed mechanically. The dye mixture was applied to cotton using the application and fixing methods of Example 1, resulting in a black shade providing outstanding fastness properties.

Example 3:

- 20 Dye (A)¹ and dye (53) were synthesised separately according to known procedures. 65 parts of reaction solution of dye (A)¹ and 35 parts of reaction solution of dye (53) were mixed and the dye mixture was isolated by spray drying. The dye mixture was applied to cotton using the application and fixing methods of Example 1, resulting in a black shade providing outstanding fastness properties.

Further examples were made achieving the same outstanding fastness properties and these are given in Table 1:

Table 1

Example	Parts dye (A)	Yellow Dye No.	Parts Yellow Dye	Red Dye No.	Parts Red dye
4	60	10	20	126	20
5	58	14	25	127	17
6	65	23	14	121	21
7	55	44	25	129	20
8	70	49	15	91	15
9	65	15	10	105	25

Example	Parts dye (A)	Orange Dye No.	Parts Orange dye
10	67	55	33
11	62	61	38
12	60	69	40

Still further (binary mixture) examples were made and when applied via the cold pad-batch application method of Example 1 achieved the same outstanding fastness properties, as shown in Table 2.

Table 2

	Example	Parts dye (A)	Yellow/Orange	Parts
			Dye No.	Yellow/Orange dye
10	15	17	10	4
	16	34	10	7
	17	17	49	3
	18	34	49	6
	19	17	44	3
15	20	34	44	6
	21	17	23	7
	22	34	23	14
	23	17	61	3
	24	34	61	6
20	25	17	53	2.4
	26	34	53	6
	27	17	67	3
	28	34	67	6
	29	17	85A	2
25	30	34	85A	4
	31	17	85B	3
	32	34	85B	6

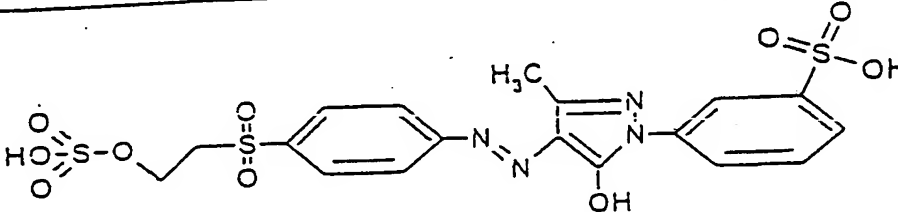
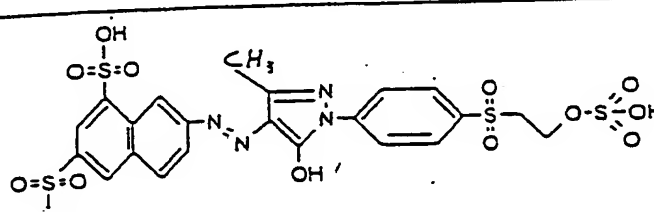
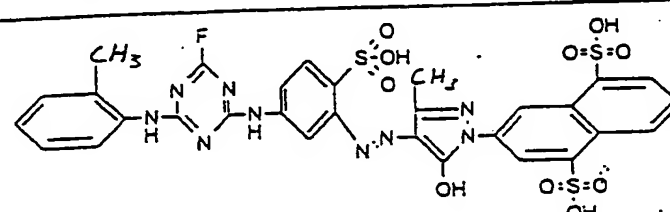
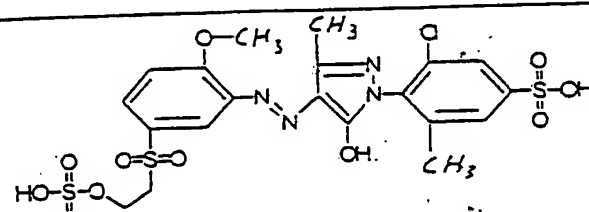
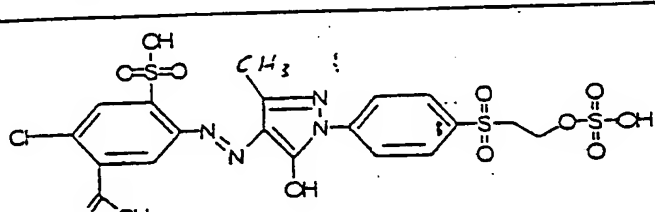
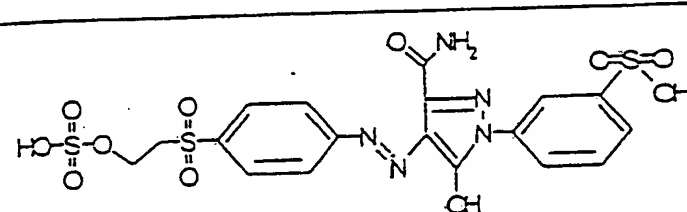
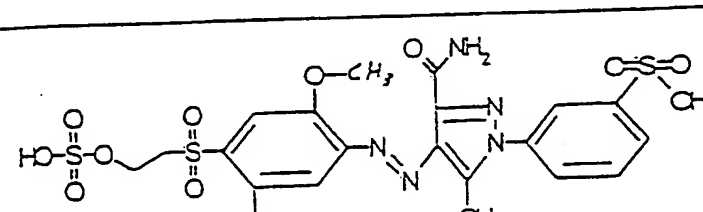
Example 13:

100g of cotton fabric was dyed according to the procedures
5 described for Example 1 using 3g of a dye mixture
containing 1.5g dye (A)¹, 0.6g dye (1), 0.3g dye (2) and
0.57g dye (94) resulting in a brown shade providing
outstanding fastness properties.

10 Example 14:

100g of cotton fabric was dyed in a dyebath that contained
1000ml water, 3g of a mixture containing 1.4g dye (A)¹,
0.13g dye (150), 0.54g dye (15), 0.30g dye (69), 0.28g dye
15 (90) and 0.35g dye (101), 15g sodium carbonate and 60g
sodium chloride. Dyeing was started at 40°C, the
temperature was raised to 60°C over a period of 20 minutes
and dyeing was continued for a further 60 minutes at this
temperature. After cooling to room temperature the dyeing
20 was rinsed and boiled with detergent resulting in a brown
shade providing outstanding fastness properties.

For each of the dyes shown in Table 2 below, dye mixtures
may be applied according to any of the procedures described
25 in Examples 1 and 14 or by similar application methods to
achieve outstanding fastness properties.

No.	Dyes	Colour on cotton
1		yellow
2		yellow
3		yellow
4		yellow
5		yellow
6		yellow
7		golden yellow

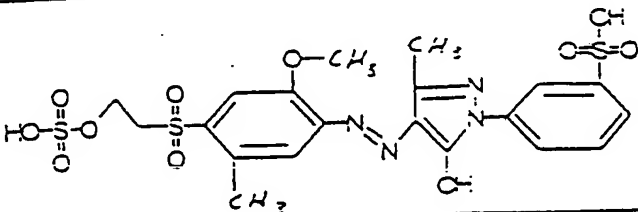
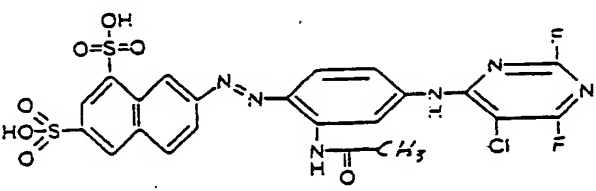
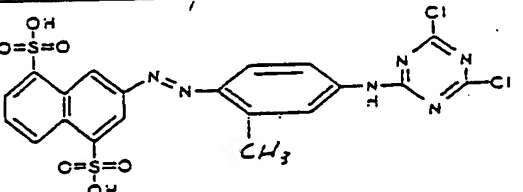
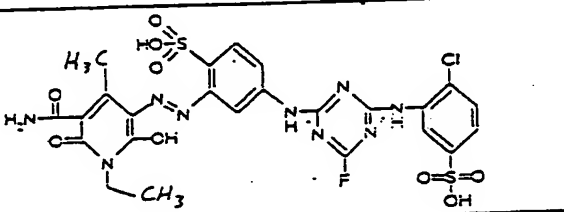
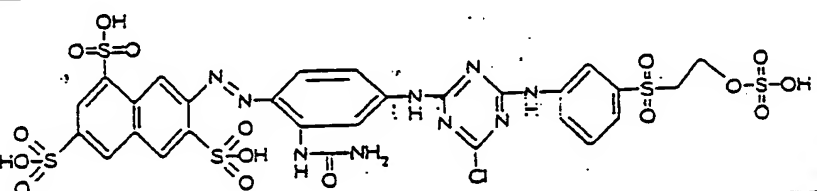
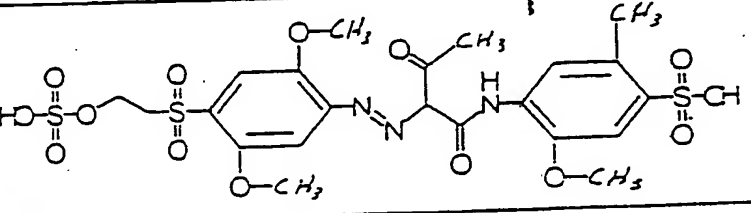
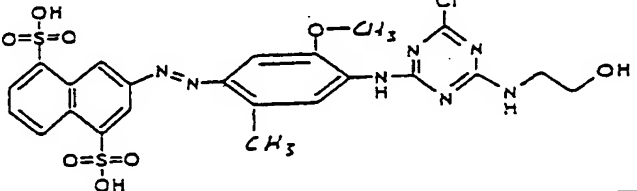
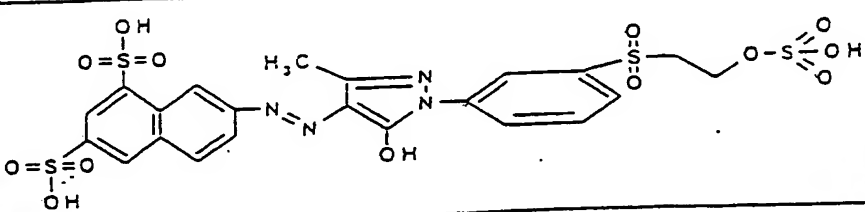
8		yellow
9		yellow
10		yellow
11		yellow
12		golden yellow
13		golden yellow
14		yellow
15		yellow

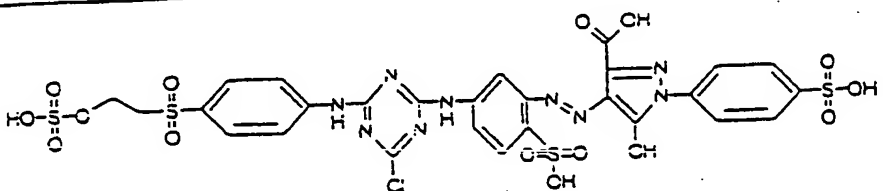
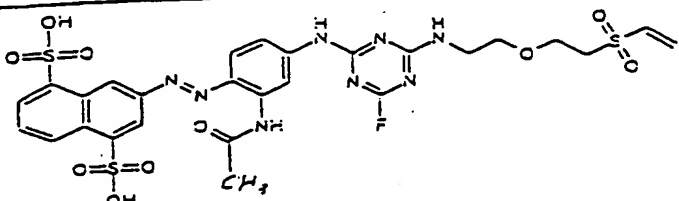
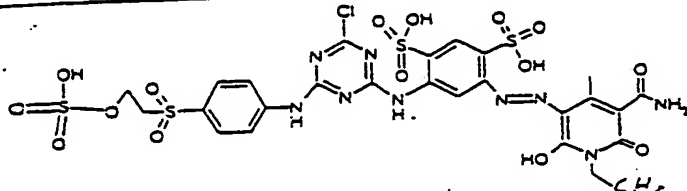
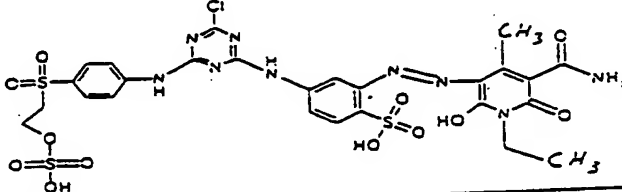
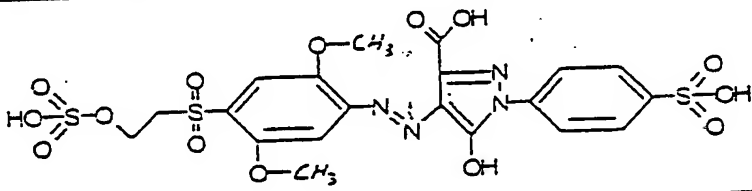
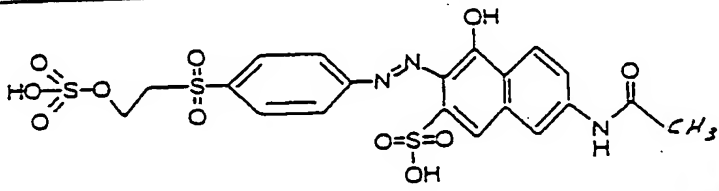
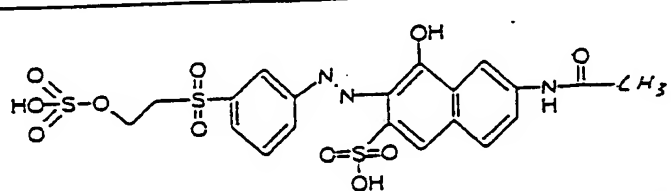
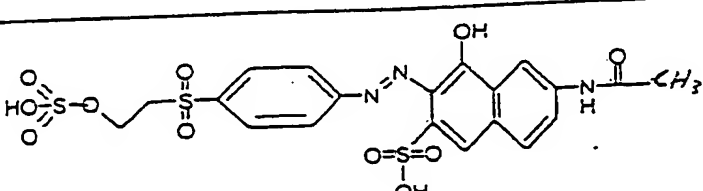
16		golden yellow
17		yellow
18		yellow
19		golden yellow
20		yellow
21		yellow
22		golden yellow
23		yellow

24		yellow
25		yellow
26		yellow
27		yellow
28		yellow
29		golden yellow
30		yellow
31		golden yellow

51

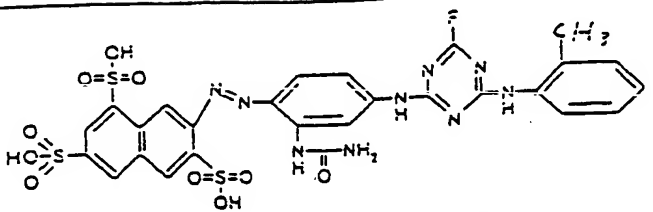
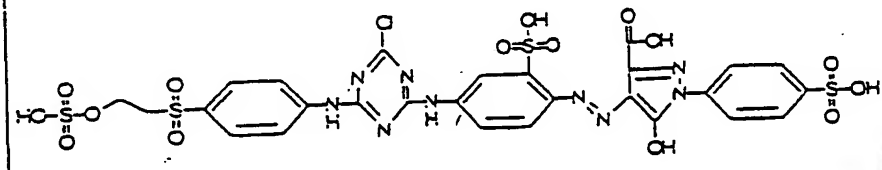
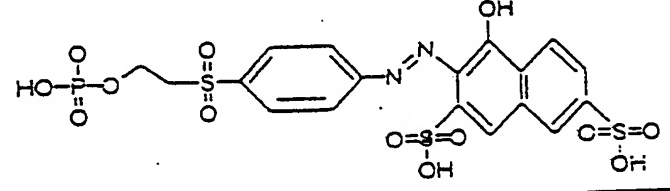
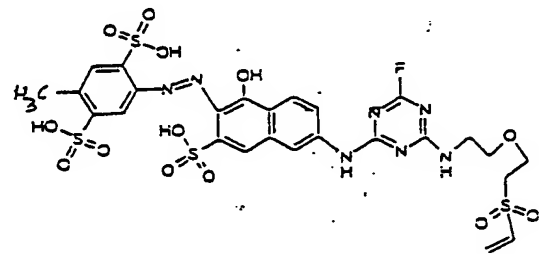
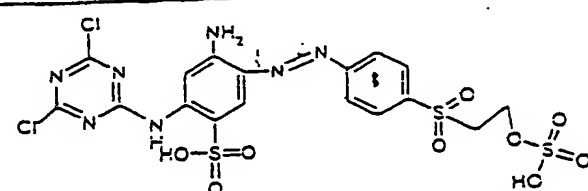
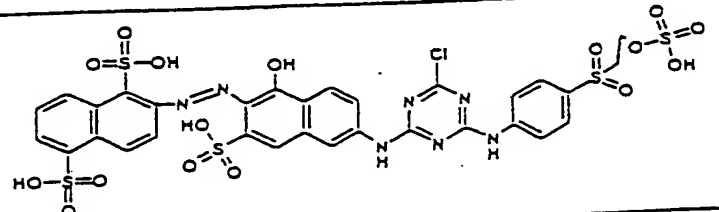
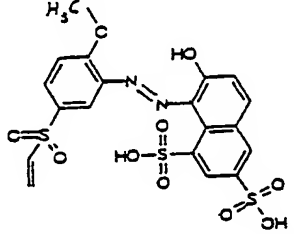
32		golden yellow
33		yellow
34		yellow
35		yellow
36		yellow
37		yellow
38		yellow
39		yellow

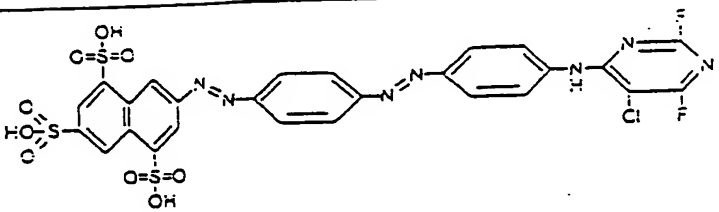
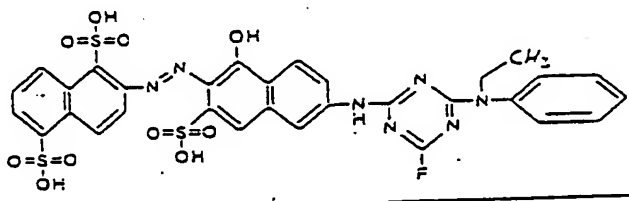
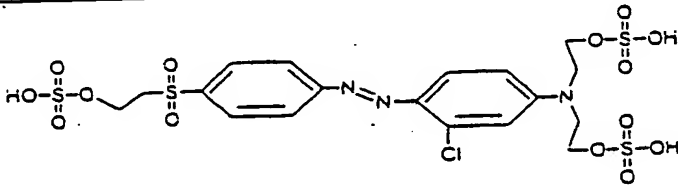
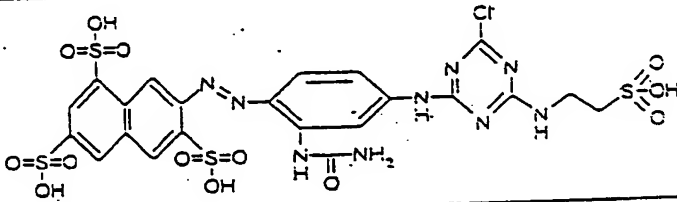
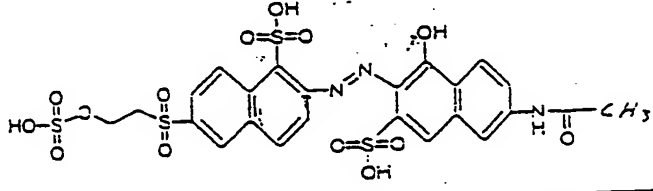
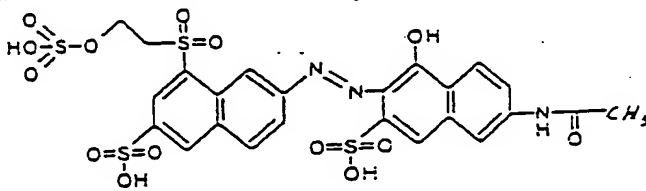
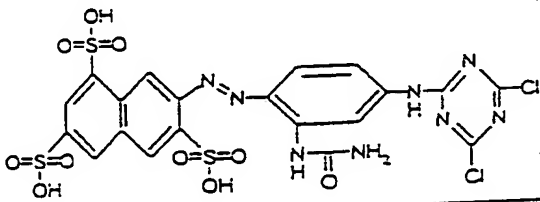
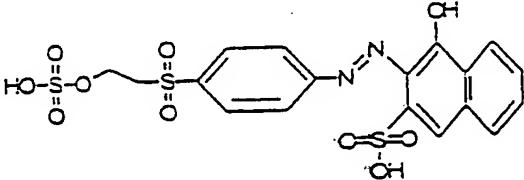
40		yellow
41		golden yellow
42		yellow
43		yellow
44		yellow
45		yellow
46		golden yellow
47		yellow

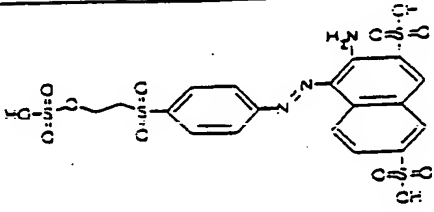
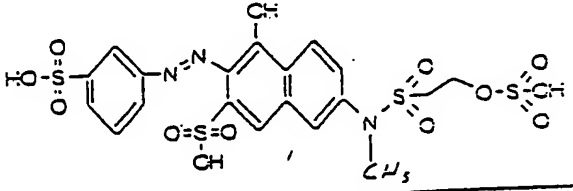
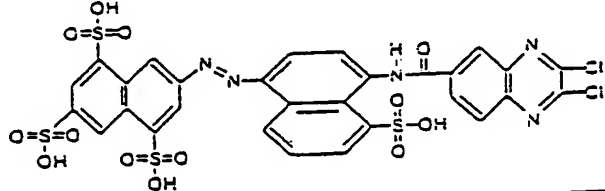
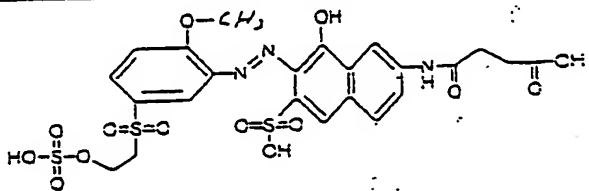
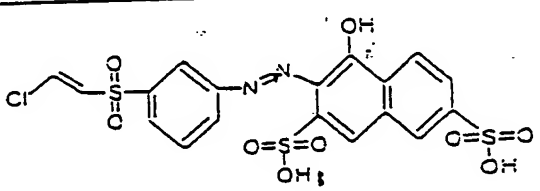
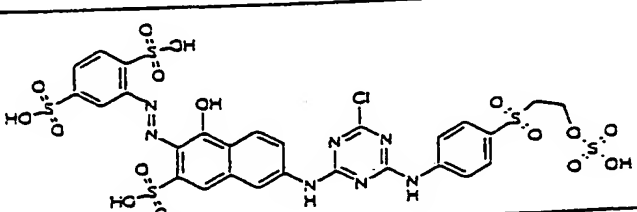
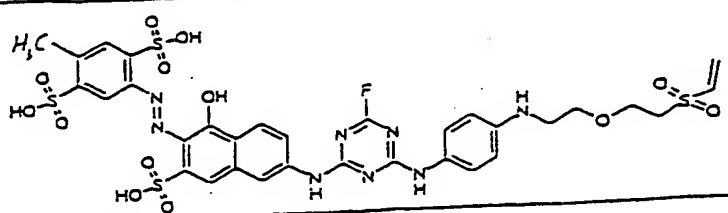
48		yellow
49		yellow
50		yellow
51		yellow
52		orange
53		orange
54		orange
55		orange

56		orange
57		orange
58		orange
59		orange
60		orange
61		orange
62		orange
63		orange

55

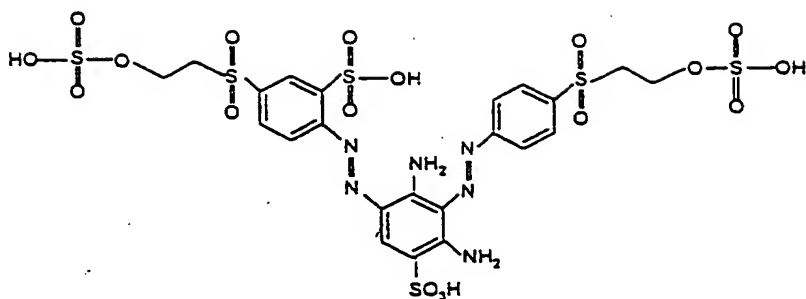
64		orange
65		orange
66		orange
67		orange
68		orange
69		orange
70		orange

71		orange
72		orange
73		orange
74		orange
75		orange
76		orange
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78		orange

79		orange
80		orange
81		orange
82		orange
83		orange
84		orange
85		orange

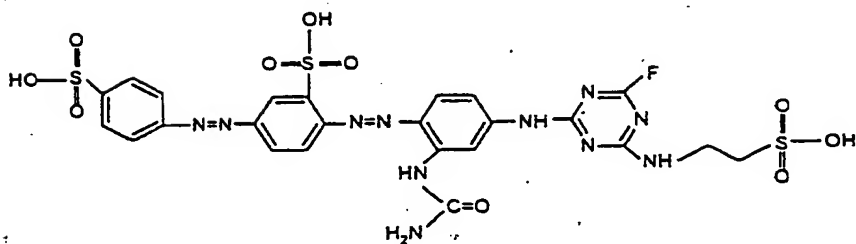
58

85A



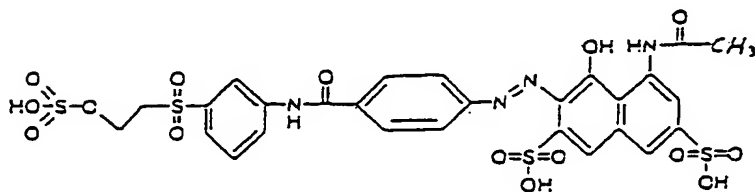
ORANGE

85B



ORANGE

86



red

59

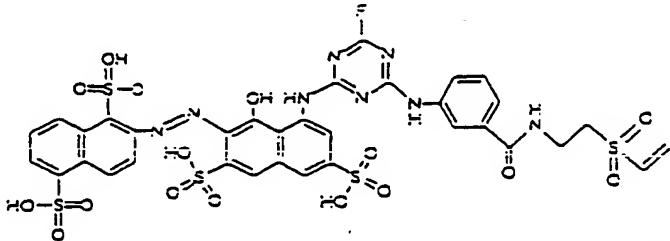
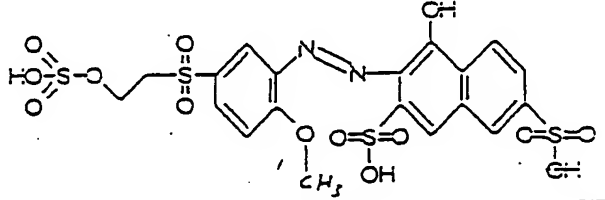
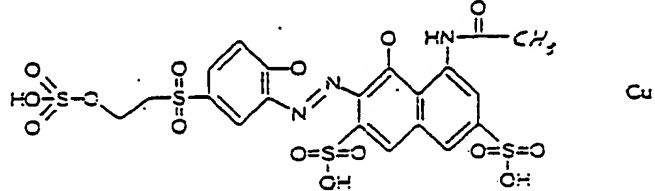
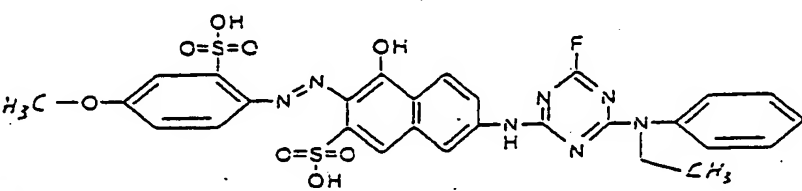
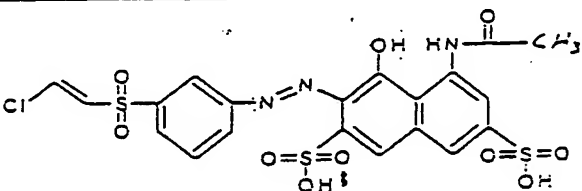
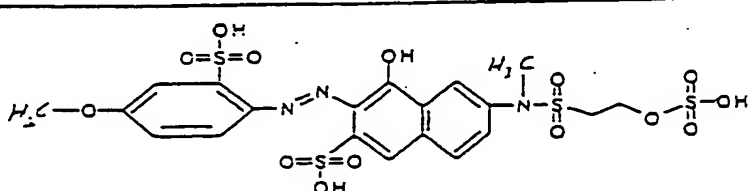
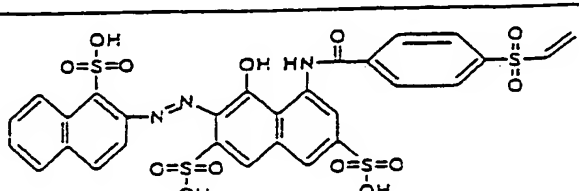
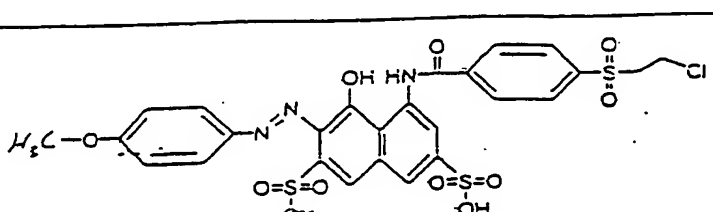
87		red
88		red
89		red
90		red
91		red
92		red
93		red
94		red



95		red
96		red
97		red
98		red
99		red
100		red
101		red
102		red

61

103		red
104		red
105		red
106		red
107		red
108		red
109		red

110		red
111		red
112		bluish red
113		red
114		red
115		red
116		red
117		red

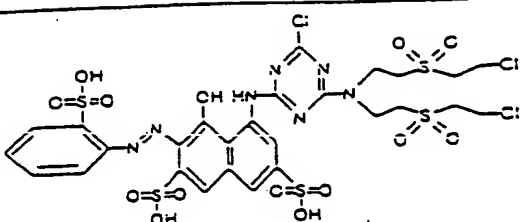
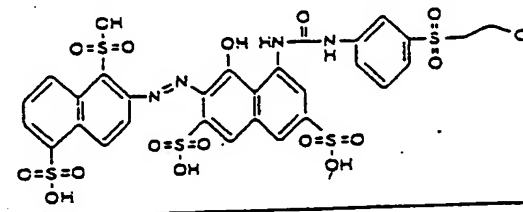
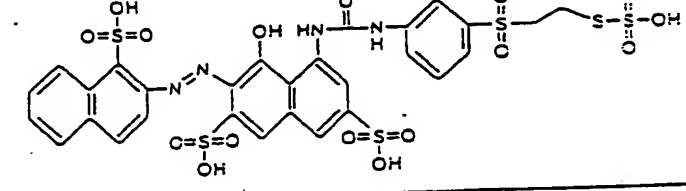
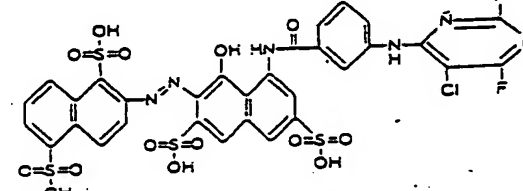
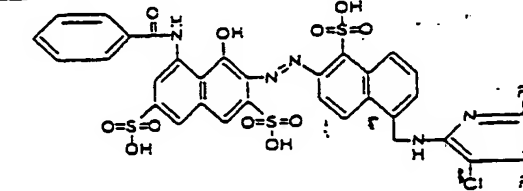
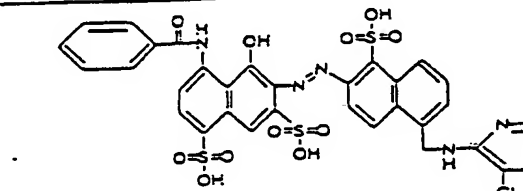
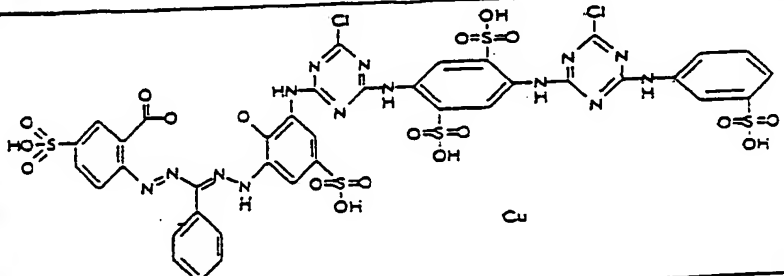
63

118		red
119		red
120		red
121		red
122		red
123		red
124		red

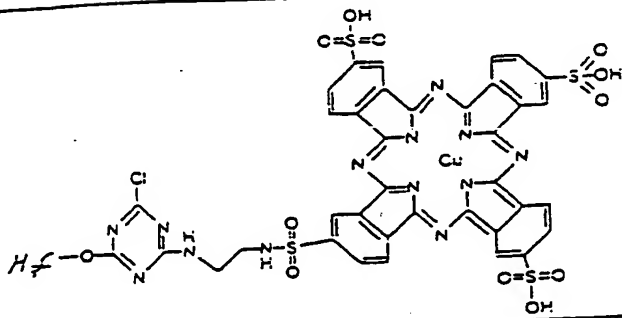
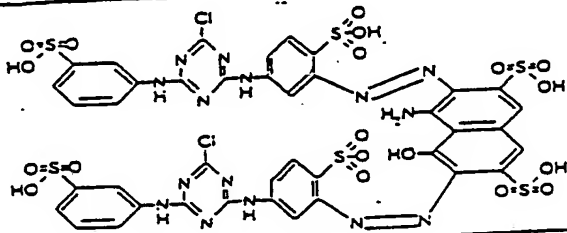
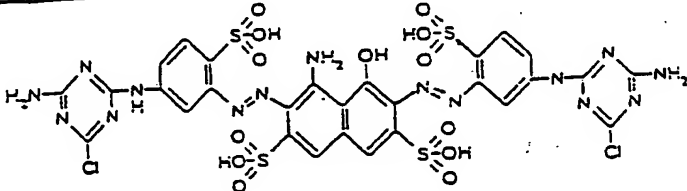
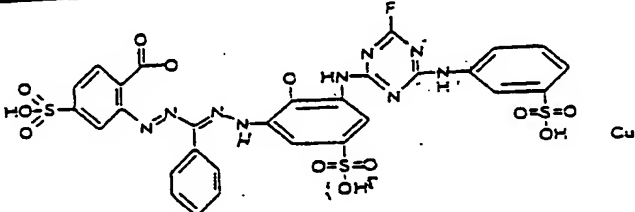
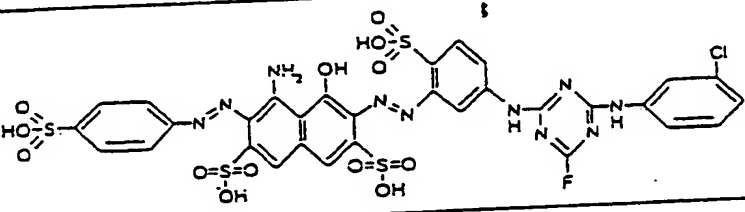
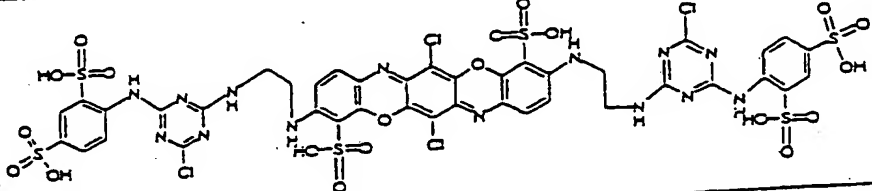
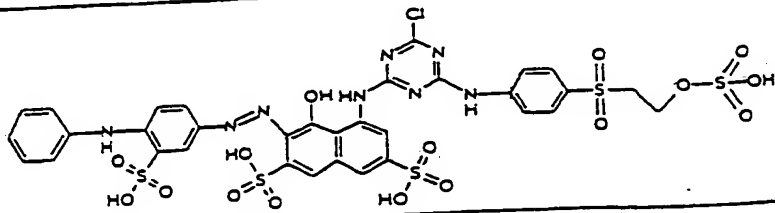
No.	Dyes	Colour on cotton
125		red
126		red
127		red
128		red
129		red
130		red
131		red

132		red
133		red
134		red
135		red
136		red
137		red
138		red
139		red

66

140		red
141		red
142		red
143		red
144		red
145		red
146		blue

67

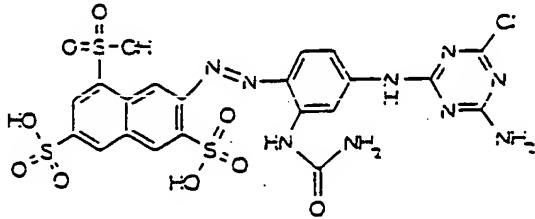
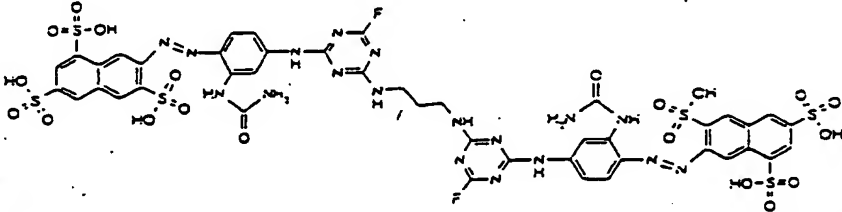
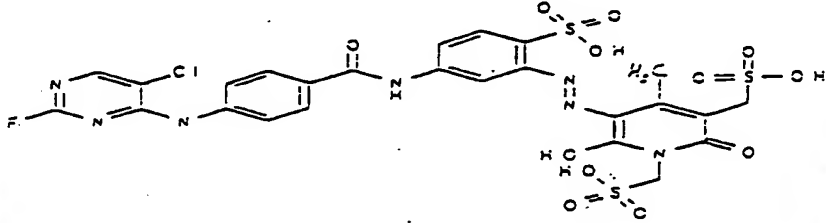
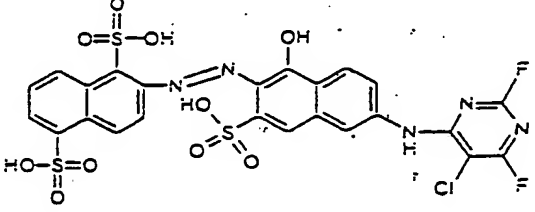
147		turquoise
148		navy
149		navy
150		blue
151		navy
152		blue
153		blue

68

154		navy
155		navy
156		navy
157		blue
158		navy
159		navy
160		blue

161		navy
162		navy
163		navy
164		navy
165		navy
166		navy
167		navy

70

168		orange
169		yellow
170		yellow
171		orange